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No. 1728.—JANUARY 6, 1893.

ON THE REACTIONS OF FERRIC SALTS WITH SULPHOCYANIDES.

By J. H. GLADSTONE, D.Sc., F.R.S.

IN the CHEMICAL NEWS for October appear the four parts of a paper by Mr. H. M. Vernon on "The Reactions of Ferric Salts with Sulphocyanides." He begins by referring to my experiments published in the *Phil. Trans.* of 1855, p. 179, which he says were made "with a view to determining whether the quantity of a salt formed in a solution was dependent on the masses of the reacting salts in accordance with the law of mass action, the importance of which was then only beginning to be thoroughly recognised." He further states: "The results obtained did not appear to obey the law of mass."

Now, the object of my paper was, as its title imports, to examine the "circumstances modifying the action of chemical affinity." I sought, in fact, to decide by crucial experiments between the then contending theories of Bergman and Berthollet; and the influence of mass was merely one of the points studied with this view. The changes of amount of a coloured salt by varying the mass of one of the colourless salts in the solution had a very important bearing on the question of reciprocal decomposition; but of course I was unacquainted with the mathematical law of mass, which was not discovered till many years afterwards by other observers.

Mr. Vernon has also apparently misunderstood my ferric sulphocyanide experiments themselves, as well as the conclusions I drew from them nearly forty years ago. On the appearance of the first instalment of his paper, I wrote to him, pointing this out. He replied expressing his regret, but in subsequent papers no correction has appeared, so I am compelled to make the correction myself. In doing so, I propose to examine his experiments and point out where they differ from, corroborate, or supplement my own.

In the first place, it is only due to Mr. Vernon to state that his investigation contains a very large amount of work, which has evidently been carefully performed; and that he has described various reactions which, as far as I know, have never been observed before. My objection is not to his experimental results, which are never in direct contradiction to my own, but to the very theoretical conclusions drawn from them.

Mr. Vernon attributes much to his method of determining the amount of ferric sulphocyanide formed, and says it differs essentially from mine. It does so; but I was acquainted with both methods. On turning to the appendix to my paper (note B, p. 222) it will be seen that after the presentation of the paper, and to meet a question

suggested by Prof. Stokes, I did make experiments in the way Mr. Vernon has adopted. On turning to Note A, p. 221, there will be found reasons for preferring the method I employed. I believed then that the horizontal method would give the truest results. I believe so still.

Mr. Vernon says that I assumed that the water added had no reducing effect on the colour of the ferric sulphocyanide beyond that due to dilution. So far from this being the case, it was well known to me, and was studied at considerable length, as will be seen at pp. 201 to 203, and p. 222. It was subsequently worked out numerically by me. (See *Quarterly Journal of the Chemical Society* for 1858, p. 36).

Effect of Increased Mass.

The experiments described in the CHEMICAL NEWS, vol. lxvi., p. 178, and the accompanying diagram, corroborate the statements of my paper in two points:—

1. That to a given dilution of a mixture of equivalent quantities of ferric salt and a sulphocyanide, the addition of further quantities of ferric salt increases the amount of ferric sulphocyanide more and more.

2. That if water be added to a mixture of ferric salt and sulphocyanide a "reduction of colour effect ensues," over and above what is due to the greater bulk of the solution.

The curves in my paper, and those in Mr. Vernon's diagram on p. 178, represent totally different phenomena. My curves always represent the increasing amount of ferric sulphocyanide produced when the proportion of one of the two salts mixed together is increased. Mr. Vernon's, on the contrary, represent the effect of different amounts of water on the ferric sulphocyanide in the several mixtures. It is this action which, he says, confirms the "law of mass." It may be so; but I cannot admit the different values which he attaches to A (the colour value at infinite concentration), in the table on p. 179, excepting that in the first column, 1:100, where the extrapolation is not carried very far. Whatever may be the case at infinite concentration, it is evident from Mr. Vernon's table that at any dilution, such as 400 litres, it is the 1:1 solution that has the least colour effect, due to ferric sulphocyanide, and 1:100 that has the most.

The assumption "that ferric chloride and potassic sulphocyanide in equivalent quantities react almost completely at infinite concentration to form ferric sulphocyanide," seems to depend upon an experiment in which he prepared such a mixture and compared it with a solution of ferric sulphocyanide, which was prepared by decomposing barium sulphocyanide by ferric sulphate. He found them to be very nearly alike in colour value.

Of course, the observation was not made at infinite concentration, or anywhere near it, but as it came into direct collision with my own view, that in such a mixture there would only be formed about 17 per cent of the possible ferric sulphocyanide, I sought for the cause of the discrepancy. It was not far to seek. In the original investigation I endeavoured to make ferric sulphocyanide by the same process, but I state that it is always impure, containing some ferrous salt and free sulphur. However, I asked Mr. Hibbert to repeat Mr. Vernon's experiment. He obtained the same result as Mr. Vernon, an approximate similarity in the depth of red colour in the two solutions; but at the same time he verified my old statement that ferric sulphocyanide so produced was very impure, and found that so far from the solution containing the theoretical quantity of ferric sulphocyanide, the red colour was greatly increased by the addition of more of either ferric chloride or potassic sulphocyanide.

There is, therefore, no reason to suppose that in a mixture of equivalent amounts of ferric chloride and potassium sulphocyanide the ordinary law of reciprocal decomposition and the usual effect of increased mass do not hold good.

Influence of the Other Radicals Present in Determining the Amount of Ferric Sulphocyanide.

In the CHEMICAL NEWS, vol. lxvi., pp. 191 and 202, Mr. Vernon describes a large number of experiments in which he mixed different ferric salts with different sulphocyanides, and that at different degrees of dilution. His results, as exhibited in the table on p. 192, are perfectly in accordance with my general views; in several respects they confirm my experiments, and in others go beyond them. They show:—

1. That the amount of red salt produced is affected by the nature of every other substance that is present in the solution.

2. That it is affected by the mass of the different substances present.

The amount produced where 100 equivalents of ferric salt are employed is invariably far greater than when the proportion is that of single equivalents. We are able to compare the mixture of equivalents of sulphocyanide of potassium with 1 and with 100 equivalents of ferric chloride at a dilution of 160 litres. They are as 18.6 to 163.4; that is, the mixture which contains a very large excess of ferric chloride gives nearly nine times as much indication of the red salt as the other one does. This difference is no doubt exaggerated by two circumstances, the effect of water being greater on the dilute than on the strong sulphocyanide solution, and the excess of undecomposed ferric chloride being itself red in colour. Still, after making due allowance for these qualifications, the results are fully confirmatory of my views on the influence of mass.

3. That the order in which the different ferric salts are decomposed by the sulphocyanide is the same as in my paper, and the proportions are nearly the same.

The following table gives the colour value of a mixture of equal equivalents of the given ferric salt and potassium sulphocyanide:—

Ferric Salt.	Colour Value.	
	Vernon.	Gladstone.
Nitrate	10.4	10.0
Chloride . . .	9.0	8.9
Sulphate . . .	7.5	6.5
Acetate	1.7	2.0

I obtained a still smaller colour value from the citrate than Mr. Vernon did, and I give no quantitative values as derived from the tartrate.

4. That the nature of the base originally combined with sulphocyanogen has a great influence on the results.

I proved this, but did not work it out quantitatively, except once in the case of hydrogen. Mr. Vernon gives

actual figures. From his table we learn that the order in which the colourless sulphocyanides are decomposed is: potassium most easily, then ammonium, sodium, calcium, and barium. We learn also that this is the case whether we are dealing with 100 equivalents of ferric salt or equal equivalents.

5. Another important matter which may be deduced from Mr. Vernon's figures is, that, for producing the coloured salt, the order of the bases is practically the same whatever may be the acid radical of the ferric salt, and the order of the acids is the same whatever may be the base of the sulphocyanide; and that this is true for both the degrees of dilution given.

Effect of Changes of Temperature.

There is a series of experiments in the CHEMICAL NEWS, vol. lxvi., p. 214, on the effect of variation of temperature upon different solutions containing ferric sulphocyanide. The changes of colour are very marked. They are not of a permanent nature, for the original degree of colour is restored on cooling. The experiments are new and interesting, but Mr. Vernon has been led astray in the explanation of them, through his having omitted to notice the effect of temperature on the excess of ferric salt not sulphocyanide. Thus, in the first six experiments, he took 100 equivalents of ferric chloride mixed with 1 equivalent of the colourless sulphocyanides of potassium, ammonium, sodium, lithium, barium, and calcium; and on heating them from 20° to 60° C., the colour was increased in each instance about 40 per cent. It is evident that each solution must have had at least 99 per cent of its iron in the condition of undecomposed ferric chloride, and, as this is itself a reddish salt, the colour of the solution must have been partially due to it. Now, on referring to my paper "On the Effect of Heat on the Colour of Salts in Solution" (*Phil. Mag.*, December, 1857), it appears that on heating its solution "sesquichloride of iron passes from orange to a deep and almost pure red."

No figures were there given, so I have thought it worth while to look into the matter a little further. It was found on experiment that not only does the ferric chloride change colour on heating, but the amount of change varies greatly with the proportion of water present and the length of time during which the heating is continued. Thus in a 3.8 per cent solution the depth of colour was about doubled at once when heated from 20° to 60° C.; while in a 0.06 per cent solution it increased fourfold. These figures are inevitably vague on account of the change of tint. It was found also that the colour of a solution containing 100 equivalents of ferric chloride at the ordinary temperature is increased about twenty-fold on the addition of 1 equivalent of potassium sulphocyanide; but when the two are compared at 60° the increase is not nearly so great.

This suggested the idea that the effect or rise of temperature on the ferric sulphocyanide might actually decrease its colour value. That this is the case is pretty evident from Mr. Vernon's observations that the actual value of a mixture of single equivalents of ferric chloride and potassium sulphocyanide (where, of course, very nearly all the colour was due to the deep red ferric sulphocyanide), was, on heating, reduced from 100 to 46.8. But the matter was tested further by heating a solution of the impure ferric sulphocyanide, obtained by the double decomposition of ferric sulphate and barium sulphocyanide. This was also weakened in colour on heating; but a better experiment was made by mixing 1 equivalent of ferric chloride with 100 equivalents of potassium sulphocyanide, when, according to the laws of reciprocal decomposition, very little undecomposed ferric chloride could have been in the solution. The colour value of the deep red salt was diminished 50 per cent on heating from 20° to 60° C.

This result, if true, is curious, as it indicates that the action of increased temperature on ferric sulphocyanide

is analogous to that of increased dilution, while in all solutions of coloured salts examined by me in 1857, I found "the increase of heat having the opposite effect to an addition of water." It is possible, however, that this reduction may be brought about by a change in the relative affinities arising from the change of temperature.

Without discussing Mr. Vernon's theoretical conclusions, it therefore appears to me that the whole of his careful experiments not only are in accordance with my old views of the reciprocal decomposition of salts in solution, but furnish some additional arguments in their favour.

ON THE ABSORPTION OF NITROGEN BY PLANTS.*

By GEORGES VILLE.

WHEN I began my experiments on the absorption of nitrogen by plants the reigning opinion attributed all the nitrogen of plants over and above that of the manures to the ammonia of the air.

The first point to solve was, therefore, to know if the air really contained ammonia, and if this ammonia occurred there in a quantity sufficient for the great part ascribed to it.

I will not again return to my determinations of ammonia, which you know; I confine myself to remind you that I devoted to this research two entire years, and that the result of sixteen determinations was, as a mean, in 100 cubic metres of air, 2.84 m.grms. Ten years later, M. Schloësing found 2.56; difference, 0.28 milligram. referred, in round numbers, to 130 kilograms. of air.

2. At the side of the apparatus which served for the determination of the ammonia there was a second apparatus consisting essentially of a glass bell in connection with a second aspirator, which conveyed into the interior of the bell a volume of air approximately equal to that which served for the determination of the ammonia in an independant apparatus placed at its side.

The following was the result of the experiment:—

Nitrogen of the crop	0.258	gram.
Nitrogen of the ammonia of the air	0.001	gram.
Nitrogen of the seed .. 0.154	..	0.155 ..
<hr/>		
Nitrogen absorbed by the plants	0.103	..

This experiment having been contested, I offered the Academy to repeat it under a commission which it should nominate. My offer was accepted. This commission, consisting of MM. Chevreul, Dumas, Payen, Regnault, Péligot, drew up the programme which I was to follow, to which I submitted without discussion.

The experiment executed at the museum consisted, in fact, of two independent experiments: the first, where the plants, cultivated in calcined sand, were shut up in a cage of metal with glass sides; the second, executed under a small glass bell, was in reality the exact copy of my former experiment of 1849.

We will first take the result of the experiment performed in the metal cage. The plant selected was cress:—

	Weight of crop. Grm.	Weight of seed. Grm.	Proportion of crop to seed.	Excess of nitro- gen in crop. Grm.
No. 1.	2.241	0.319	7 times	0.000
No. 2.	1.506	0.127	11 ..	0.007
No. 3.	5.021	0.124	48 ..	0.050

We see that the experiment consisted of three independent cultivations in separate pots, all three plunged in the same basin of distilled water.

* Extracts from a letter to the Editor.

Nitrogen.

	In crop. Grm.	In seed. Grm.	Proportion of nitrogen in the crop to that in seed.	Nitrogen drawn from the air. Grm.
No. 1.	0.0097	0.0099	Equal	0.000
No. 2.	0.011	0.0039	2.9	0.007
No. 3.	0.053	0.0038	13.9	0.050

From reasons which it is needless to recal, the commission decided that a second experiment subsidiary to the former should be made. To this end, a small glass bell was fixed, in which there should be only a single cultivation of cress in calcined sand, the air of the metal cage passing into the small bell before entering the aspirator. This was, in fact, making separate experiments with the same air. The following was the result of the second experiment:—

Experiment of 1853 on Cress.

Weight of crop	3.60	gram.
Weight of seed	0.206	..
Proportion of crop to seed	17.4	..

Nitrogen.

In crop	0.0035	gram.
In seed	0.035	..
Proportion of N in crop to that of seed	5.5	..
N drawn from air	0.0287	gram.

The second experiment concluded like the former. I consider it the purest and most irreproachable that has ever been performed, considering that there were employed only 500 grms. calcined sand and a litre of distilled water, which scarcely contained 0.0001 of nitrogen!

But what gives it for me an inestimable value is that it reproduces, term for term, my experiment of 1849 in a limit of approximation of which, to my knowledge, the history of vegetable physiology offers no instance.

Permit me to introduce here my experiment of 1849, as I have given that of 1853, to render the comparison easier and more striking:—

Weight of crop	8.13	gram.
Weight of seed	0.531	..
Proportion of crop to seed	16.6	..

Nitrogen.

In crop	0.147	gram.
In seed	0.026	..
Proportion of N in crop to that of seed	5.6	..
N derived from air	0.108	..

Finally, these are the experiments which M. Bréal, the assistant of M. Dehérain, has just verified, placing himself, in my opinion, in conditions much less rigorous than those in which I operated.

The year 1853 was one of the most harassing of my life. When I asked the commission for a locality for the experiment of control, I was shown, in Rue Paliveau, at the extremity of the nursery grounds of the museum, a vague plot where there was neither a house, nor buildings, nor water. I had to construct everything: a shelter for my aspirator—a shed, the walls and the roof of which were bitumenised paper. To work my aspirator, I had to construct an artificial reservoir. I was then living at the opposite extremity of Paris, in the suburb of Grenelle, at a distance of 8 kilometres from the museum, which I had to traverse twice daily.

In an early letter I will explain to you three demonstrations of the absorption of nitrogen of a different character which I have produced. This I can do the

more easily, as the library of the Royal Society contains my "Recherches Experimentales," edition in 4to., of 1853, and the more complete 8vo. edition of 1868.

SOME RESULTS AND CONCLUSIONS DERIVED FROM A PHOTOGRAPHIC STUDY OF THE SUN.

By GEORGE E. HALE.

IN view of the fact that the study of prominence, facula, and sun-spot spectra by photographic means has now been taken up by several investigators, it seems desirable to bring together the results of the work in this direction which has been in progress at the Kenwood Observatory since April, 1891. Some of these results have been published before or casually referred to in papers on other branches of solar work, but they cannot fail to be of greater value for comparison with the investigations of others if grouped in a single article. There also remain to be mentioned several disconnected matters to which attention has not yet been called.

The following are some of the results, with several conclusions to which I have been led; further investigations may very possibly render necessary material modifications in the views here expressed.

Chromosphere and Prominences.

1. H and K are always present as the strongest lines in the chromosphere and prominence spectrum.
2. These lines extend to the highest parts of all prominences, but have not yet been traced to any greater distance from the limb, *i.e.*, into the corona.
3. K seems to be invariably stronger than H, and extends farther from the limb.
4. In cases of motion in the line of sight the distorted forms of the H and K lines are similar.
5. Prominences have the same form in both lines. Where apparent differences exist they may probably be ascribed to the greater brightness of K. (This remark also applies to 4).
6. Both H and K expand rapidly in width from the upper surface of the chromosphere to its base. Consequently photographs taken with the slit just tangent to the limb show these lines more than twice as broad as they appear in the higher regions of prominences.
7. Both lines are often doubly reversed (narrow dark lines running down the centre of the bright lines) in the chromosphere, and sometimes in the base of bright prominences.
8. H is always accompanied by a hydrogen line ($H\epsilon$), but this line is much fainter, and does not extend so high in prominences.
9. The entire series of ultra-violet hydrogen lines have been photographed in very bright prominences, but in faint prominences the lines more refrangible than α_1 or β_1 are usually absent from the photographs. They may, however, be present as very faint lines in all prominences, but remain invisible on the photographs on account of the brilliancy of the atmospheric spectrum.
10. The line α_1 is frequently accompanied by a line slightly more refrangible, which is probably not due to hydrogen. In a few cases α_1 has been single in certain parts of a prominence, and double in other parts.
11. The upper component of α_1 is sometimes doubly reversed in the chromosphere.
12. No prominence has yet been found which showed the H and K lines alone, *i.e.*, without some of the less refrangible hydrogen lines.
13. The forms of prominences as observed in C and in H and K seem to be the same, though they may be more extensive in the latter lines.
14. Prominences seem to have the same motion in the

line of sight, whether observed in C or in H and K. (In one case where the motion of the entire prominence was considerable, a large number of lines in the ultra-violet, all that were visible on the photograph, were equally displaced with H and K).

15. The spectra of eruptive prominences frequently contain many metallic lines in the ultra-violet; notably the magnesium triplet at $\lambda 383$. (See my article on "The Ultra-Violet Spectrum of the Solar Prominences").

16. Eruptive prominences sometimes exhibit a continuous spectrum in the ultra-violet.

17. Prominences frequently show evidences of spiral motion.

Faculae.

18. Both H and K are always reversed in faculae.

19. These reversals are usually (if not invariably) double, a narrow dark line running down the centre of the broader bright line. The appearance on the photograph is consequently as if there were two narrow bright lines separated by a narrow dark line, in the centres of the broad dark shades at H and K. In some instances I have noticed that one of these narrow bright lines was missing in certain portions of a facula, an unsymmetrical double reversal resulting.

20. Distortions in the doubly reversed H and K lines of the faculae are rare. I have found but one or two instances of this kind, and in these cases the distortions took the form of expansions in the lines.

21. H is usually unaccompanied by the slightly less refrangible hydrogen line, referred to above as being always present in prominences. In a few cases, however, this line has been found extending across spots, and for some distance in the faculae on either side.

22. Neither α_1 nor any other bright lines more refrangible than H and K have been found in faculae or spots.

23. Curved forms predominate in faculae, and suggest some relation with spiral forms in prominences.

Spots.

24. The bright H and K lines seem to invariably extend entirely across every sun-spot. Both lines are doubly reversed in the faculae which probably completely surround every spot. In the umbra the reversals are narrower, and the dark central line is usually absent.

25. Small spots, especially when members of a group containing large spots, are frequently completely covered with faculae.

26. In the ultra-violet spectra of spots the dark lines of the solar spectrum do not seem to undergo selective widening, as in the less refrangible parts of the spectrum. Beyond the presence of the bright H and K lines, and the infrequent appearance of $H\epsilon$, the spot spectrum seems to differ from the ordinary solar spectrum only by the increased general absorption.

27. Distortions of the bright H and K lines in spots are extremely rare.

Conclusions.

28. The exact agreement of H and K with the two strongest lines in the spectrum of the calcium spark leads me to attribute these prominence lines to calcium. While the properties of calcium in its terrestrial condition make it difficult to see how its vapour can form the most important constituent of the prominences, yet I do not see how we are to escape from this conclusion.

29. No other than a negative conclusion can as yet be offered in regard to the perplexing question of the so-called "white prominences." At the eclipse of August 29, 1886, a large prominence was photographed which was said by Professor W. H. Pickering to have no other lines in its spectrum than H and K, and a faint trace of an ultra-violet line, in addition to a bright continuous spectrum. He goes on to add (*Annals of Harvard College Observatory*, vol. xviii., No. 5, p. 100): "It was therefore quite invisible, both before and after totality, by the usual spectroscopic method, as was in fact noted at the time by

Professor Tacchini." The character of the photograph, at least so far as can be judged from the reproduction accompanying the report, was hardly such as to warrant any very positive statement as to the absence of the hydrogen lines, particularly as they might have been partly obscured by the bright continuous spectrum. The prominence might also have been eruptive in nature, not lasting longer than the duration of totality, and thus may not have existed when Professor Tacchini made his observations before and after the eclipse. However, this may be, for this is only one of a number of cases in which "white prominences" have been recorded, I have as yet found no prominences which exhibited H and K without the hydrogen lines. This point has not been made the subject of special investigation, however, and it may be that some cases of the kind may ultimately be brought to light.

30. The fact that small spots are sometimes completely covered with faculous matter (or possibly with prominences) may assist in explaining the anomalous heat radiations recently measured in certain spots by Professor Frost (*Astronomy and Astro-Physics*, October, 1892). I hope to take up this point more in detail elsewhere.

31. Photographic methods have abundantly substantiated the conclusions long ago drawn from visual observations in regard to the nature of faculæ. In a great many photographs taken with the spectroheliograph, faculæ are shown projecting above the sun's limb. And the intimate relationship between faculæ and eruptive prominences is not less evident, especially in composite photographs showing faculæ and prominences on the same plate. When we consider that eruptive prominences probably arise from faculæ, it is not at all surprising that such prominences sometimes show a continuous spectrum in addition to their bright lines. For a violent eruption would naturally carry up with the prominence some "dust-like" (See Fényi, *Astronomy and Astro-Physics*, May, 1892, p. 431) matter from the faculæ, which would give a continuous spectrum.

32. The reversals of the H and K lines over spots seem to be readily explainable. As has been stated above, the reversals are double in the penumbra, and also for a considerable distance on either side of the spot, but usually single in the umbra. As spots seem to be always surrounded by faculæ, which frequently encroach upon the penumbra, the double reversals occur in these just as they do in faculæ not in the vicinity of spots. The single reversals in the umbra, however, probably take their rise in the chromosphere, which presumably overlies the cooler regions of the spot.—*Astronomy and Astro-Physics*, No. 109.

REPORT ON THE TECHNICAL DETERMINATION OF ZINC.*

IN accordance with the plan outlined some time since, your committee appointed for the purpose has undertaken the work of attempting to establish a uniformity in the technical methods of analyses in the West, and as the result of its first effort it herewith presents to your body the work of a number of our best known western chemists on zinc determination.

It may be remarked that the samples of ore on which the work was done were such as seemed to offer the greatest difficulty in the correct determination of the metal in question.

The ores so submitted were from a number of mines of widely separated localities; they were mixtures of galenite, pyrite, and sphalerite, accompanied by greater or less percentages of manganese in the form of rhodochrosite, associated with a quartzose gangue.

That a standard of comparison might be had by which

the various results could be judged, the assistance of the chemical laboratory of the U.S. Geological Survey at Washington, D.C., was invoked. Mr. F. W. Clarke, Chief Chemist of the Survey, notwithstanding the fact that his department is always busily engaged with work correlated to the geological investigation of the survey, met our request for the co-operation of his laboratory in the work to be undertaken with the greatest willingness, and your committee takes this occasion to express its deep appreciation of the valued assistance thus afforded.

The analyses were made by Mr. L. G. Eakins, one of the ablest of Mr. Clarke's corps of chemists, and your committee does not doubt that the results furnished by him will unhesitatingly be accepted as standard by all the technical chemists who assisted in the investigations.

The samples of ore distributed came from the following mines:

Enterprise Mine, at Rico, Colorado.

Mary Murphy Mine, near St. Elmo, Colorado.

Robinson Mine, Robinson, Colorado.

New York Mine, near Park, Colorado.

Moyer Mine, Leadville, Colorado,—the ore from this property being a concentrate product.

These were designated, respectively, Nos. 5, 9, 11, 13, and 20, great care being taken in the mixing of each separate large sample, so that uniformity in the material subsequently distributed might be assured.

The analytical methods employed by the different chemists are given, together with the results obtained. In one instance, that of Dr. H. C. Hahn, in conjunction with the zinc determination, that of manganese is also furnished, thus happily affording a knowledge of the extent to which the latter element was present.

Method of L. G. Eakins, Chemist U.S. Geological Survey, Washington, D.C.—About one gm. of ore was treated with twenty-five c.c. of dilute hydrochloric acid (1 : 1) and after digestion on the water bath three c.c. of nitrate acid were added, the whole being then evaporated to dryness. The dried mass was digested with dilute hydrochloric acid and water, and the insoluble residue filtered off. The filtrate was precipitated with hydrogen sulphide, filtered, and the precipitate re-dissolved in nitrohydrochloric acid, evaporated nearly to dryness, and water and hydrochloric acid added.

This solution was once more precipitated with hydrogen sulphide, the precipitate filtered off, washed, and the filtrate combined with the first. The solution was now oxidised with nitric acid, and a basic acetate precipitation made. The resulting precipitate was filtered off, dissolved in dilute hydrochloric acid, and re-precipitated as basic acetate, filtered, and this precipitate again dissolved. This solution was evaporated to expel excess of acid, and then poured with constant stirring into an excess of strong, cold ammonia, the precipitate allowed to stand for some time, after which it was filtered off and washed.

The solution from the last ammonia precipitation was found in every case to still contain zinc which had not been removed by the two previous basic acetate precipitations, the amount so held varying from 0.30 per cent. to 2 per cent.

The filtrates from the basic acetate precipitations were combined, evaporated to a convenient bulk, about 5 grms. of acetate of sodium and five c.c. of glacial acetic acid added, the solution heated to boiling, and the zinc precipitated with hydrogen sulphide. The precipitated sulphide was allowed to settle, the solution filtered, and the precipitate washed with hydrogen sulphide water containing acetate of sodium.

The filtrate obtained from the ammonia precipitate was now evaporated to expel excess of ammonia, acetate of sodium and glacial acetic acid added, and the zinc precipitated as sulphide in the same way as has just been described.

The zinc sulphide precipitates were combined and digested with dilute hydrochloric acid containing hydro-

* A report read at a meeting of the Colorado Scientific Society.

gen sulphide. All arsenic and traces of nickel (if present) were left undissolved, the zinc and any cadmium that might be present passing into solution. This solution was filtered, the filtrate evaporated to expel the hydrogen sulphide, and the zinc precipitated as carbonate with carbonate of sodium in the usual way, being finally weighed as oxide of zinc.

This was dissolved in dilute hydrochloric acid, the small amount of silica which may have contaminated the precipitate filtered off, washed, and weighed.

To the filtrate an excess of tartaric acid was added, then an excess of caustic soda, and after the solution was diluted to a large bulk it was boiled in a platinum dish to precipitate any cadmium which might have been associated with the oxide of zinc. The precipitate so obtained was filtered off, washed, and weighed, and correction made for such amount, together with what silica had previously been found.

The result were as follows :

No. 5	14.64	per cent. zinc.
" 9	24.11	" " "
" 11	10.71	" " "
" 13	6.31	" " "
" 20	16.09	" " "

Note : Sample number five contained appreciable quantities of cadmium, sample number nine very small quantities, and the other samples only traces of this element.

Method of Messrs. von Schulz and Low, Chemists and Assayers, Denver, Colorado.—Prepare a solution of ferrocyanide of potassium by dissolving 44 grms. of pure salt in distilled water and diluting to one litre. Standardise as follows :—

Dissolve exactly 200 m.grms. of pure oxide of zinc in a beaker in ten c.c. of strong pure hydrochloric acid. Now add 7 grms. of C. P. chloride of ammonium (the commercial article frequently contains a little copper), and about a hundred c.c. of boiling hot water. Titrate the clear liquid with the ferrocyanide solution until a drop, when tested on a porcelain plate with a drop of a strong aqueous solution of acetate of uranium, shows a brown tinge. About sixteen c.c. of ferrocyanide will be required, and accordingly nearly this amount may be run in rapidly before making a test, and then the titration finished carefully by testing after each additional drop of ferrocyanide. As soon as a brown tinge is obtained note the reading of the burette, and then wait a minute or two and observe if one or more of the previous tests do not also develop a brown tinge. Usually the end-point will be found to have been passed by a test or two, and the proper correction must then be applied to the burette reading. Finally make a further deduction from the burette reading of the amount of ferrocyanide required to produce a brown tinge under the same conditions when no zinc is present. This correction is about two drops, or 0.14 c.c.

200 m.grms. of oxide of zinc contain 160.4 m.grms. of zinc, and one c.c. of the above standardised solution will equal about 0.01 gm. of zinc, or about 1 per cent. when 1 gm. of ore is taken for assay.

Prepare the following solutions for the assay of ores :—

A saturated solution of chlorate of potassium in nitric acid, made by shaking an excess of the crystals with the strong pure acid in a flask. Keep the solution in an open flask.

A dilute solution of chloride of ammonium containing about 10 grms. to the litre. For use heat to boiling in a wash bottle.

A wash bottle of hot water.

Take exactly 1 gm. of the ore and treat in a 3½ inch casserole with twenty-five c.c. of the above chlorate solution. Do not cover the casserole at first, but warm gently until any violent action is over and greenish vapours have ceased to come off. Then cover with a watch-glass and boil rapidly to complete dryness, but avoid over-heating and baking. A drop of nitric acid adhering to the cover

does no harm. Cool sufficiently and add 7 grms. of chloride of ammonium, fifteen c.c. of strong ammonia water, and twenty-five c.c. of hot water. Boil the covered mixture one minute, and then, with a rubber-tipped glass rod, see that all solid matter on the cover, sides, and bottom of casserole is either dissolved or disintegrated. Filter into a beaker and wash several times with the hot chloride of ammonium solution. A blue-coloured filtrate indicates the presence of copper. In that case add twenty-five c.c. of strong pure hydrochloric acid and about 40 grms. of granulated test-lead. Stir the lead about in the beaker until the liquid has become perfectly colourless and then a little longer to make sure that the copper is all precipitated. The solution, which should still be quite hot, is now ready for titration. In the absence of copper the lead is omitted and only the acid added. About one-third of the solution is now set aside, and the main portion is titrated rapidly with the ferrocyanide until the end-point is passed, using the uranium indicator as in the standardisation. The greater part of the reserved portion is now added, and the titration continued with more caution until the end-point is again passed. Then add the remainder of the reserved portion and finish the titration carefully, ordinarily by additions of two drops of ferrocyanide at a time. Make corrections of the final reading of the burette precisely as in the standardisation.

Gold, silver, lead, copper, iron, manganese, and the ordinary constituents of ores do not interfere with the above scheme. Cadmium behaves like zinc. When known to be present it may be removed, together with the copper, by the proper treatment with hydrogen sulphide, and the titration for zinc may be made upon the properly acidified filtrate without the removal of the excess of gas. There seems to be no simpler way to remove cadmium.

The following results were obtained on the samples of ore sent us by the Colorado Scientific Society. Each sample was assayed only once. The weighing was done on the ordinary ore-scale and the burette used had not been corrected. It was intended to show just what would be obtained by the method in ordinary technical work.

Sample No. 5.. ..	15.31	per cent. zinc.
" " 9.. ..	24.34	" " "
" " 11.. ..	10.76	" " "
" " 13.. ..	6.42	" " "
" " 20.. ..	16.14	" " "

Notes on the above scheme :

Acids destroy the delicacy of the uranium test, and for this reason a strong aqueous solution of uranium acetate is used. By having the zinc solution only faintly acid the production of the brown colour in the end test becomes almost instantaneous and no previous test will develop a colour. Under these conditions, however, lead is apt to seriously interfere, and the excess of acid recommended above is found to be a necessity. When a strong solution of uranium acetate, not acidified, is used as indicator, the error caused by the excess of acid in the zinc solution amounts to only two drops of ferrocyanide, which may be allowed for, and the brown tinge develops so rapidly that the end-point is seldom passed by more than one test.

When an ore contains but little copper, the granulated lead used frequently coheres in lumps that may hold zinc solution. These lumps are most easily broken up after a little of the ferrocyanide has been added. They appear to cause no appreciable error in the work. Of course, lead shot or thin sheet lead may be used if preferred, and it may be cleaned with strong nitric acid and used repeatedly. It seems simpler and more satisfactory, however, to use the granulated lead and throw it away after use.

As regards the effect of nitric acid, it is found that the addition of one c.c. of the strong acid to the boiling hot zinc solution during the standardisation of the ferrocyanide makes no appreciable difference.

Method of Mr. L. W. W. Jones, Chemist Pueblo Smelting and Refining Company, Pueblo, Colorado.—The method used was that published some time since by Messrs. von Schulz and Low, Chemists and Assayers, Denver, Colorado, which consists in effecting a decomposition of the ore by means of concentrated nitric acid saturated with chlorate of potassium, evaporating to dryness, and bringing the zinc into solution by means of water, ammonia water, and chloride of ammonium; heating the solution to boiling, filtering off the insoluble residue, and washing. If the filtrate shows the presence of copper, this metal is precipitated after acidifying the solution with hydrochloric acid by means of granulated lead.

To the hot solution a few grms. of sulphite of sodium are now added to counteract any effects due to the possible present of free chlorine from the action of the hydrochloric acid on any chlorate that might not have been decomposed, and the zinc titrated with a standardised solution of ferrocyanide of potassium, using acetate of uranium as an indicator.

The readings of the burette were corrected by an amount of ferrocyanide necessary to produce a reaction with acetate of uranium in a blank test, the standardisation having been made under like conditions.

The results obtained on the samples submitted were:—

No.	5..	15.39	per cent.	zinc.
"	9..	24.53	"	"
"	11..	10.83	"	"
"	13..	6.58	"	"
"	20..	16.46	"	"

Method of Mr. E. N. Hawkins, Superintendent Holden Smelting and Refining Company, Leadville, Colorado.—One gm. of ore is treated in a 3½ inch casserole with five to ten c.c. of concentrated nitric acid, evaporated to dryness on a hot plate and baked for several minutes. After cooling, twenty to thirty c.c. of water are added, and about 7 grms. of chloride of ammonium and fifteen c.c. of strong ammonia water.

If the ore is free from manganese proceed as follows:—

Boil for several minutes, filter and wash with warm water, taking the precaution to add a few drops of ammonia water to the first wash water on filter to keep the zinc in solution. It is more convenient to operate in this way than to use ammoniacal wash water.

Neutralise the filtrate with hydrochloric acid, then add an excess of ten c.c. of the acid. If copper is present precipitate it with granulated lead.

The solution is now ready for titration with ferrocyanide of potassium, uranium acetate being used as an indicator.

If manganese is present, after addition of chloride of ammonium and ammonia water as stated above, add to the solution five c.c. of peroxide of hydrogen and boil. The manganese will all be precipitated as the hydrated dioxide together with such iron and alumina as may be present. Filter, using the regular precautions.

Now dissolve the precipitate in a small quantity of hydrochloric acid, dilute with water, add an excess of ammonia water and again five c.c. of peroxide of hydrogen, boil for several minutes, filter and wash, and combine filtrate with the one previously obtained.

The solution is now made acid with an excess of hydrochloric acid, and the titration of the zinc effected, after removal of any copper that may be present, as previously specified.

In ordinary practice it has been found that the amount of zinc which is carried down with the manganese in its first precipitation by means of peroxide of hydrogen, in the ores which carry from 3 to 10 per cent. of that element, is equal to about 5 per cent. of the total quantity of zinc present, although this does and will vary somewhat with different practice and the amounts of reagents employed.

The results obtained were as follows:—

No.	5..	15.66	per cent.	zinc.
"	9..	24.23	"	"
"	11..	11.88	"	"
"	13..	8.73	"	"
"	20..	15.86	"	"

Method of Mr. F. C. Knight, F.C.S., Chemist, Boston and Colorado Smelting Company, Argo, Colorado.—1 gm. of ore is taken and mixed in a 3½ inch casserole with 10 grms. of nitrate of ammonium and ten c.c. of concentrated nitric acid added. The casserole is covered with a watch-glass and the mixture evaporated to complete dryness on a hot plate. The mass usually deflagrates just before becoming completely dry.

After cooling, about twenty c.c. of water and 5 grms. of chloride of ammonium are added.

If manganese is present, of which previous indication will have been afforded, add to the solution five c.c. of peroxide of hydrogen and ten c.c. strong ammonia water, heat to boiling for two or three minutes, filter, and wash with water containing ammonia water.

As the precipitate of iron and manganese carries zinc, it is re-dissolved in a small quantity of hydrochloric acid, water and chloride of ammonium added, then five c.c. peroxide of hydrogen and ten c.c. ammonia water as before. Boil, filter, and wash with hot water rendered ammoniacal, and combine the two filtrates. The second precipitation of the iron and manganese practically brings all zinc into solution.

The filtrate should now measure from two hundred and fifty to three hundred c.c. It is slightly acidified with hydrochloric acid, and if copper is present it is precipitated with granulated lead.

To the solution now add an excess of ten c.c. hydrochloric acid and titrate the zinc with a standardised solution of ferrocyanide of potassium, one c.c. of which is equal to about 5 m.grms. or 0.50 per cent. zinc. Acetate of uranium is used as an indicator of final reaction.

As about five to six drops of the ferrocyanide solution will be absorbed in a blank test before the reaction with acetate of uranium manifests itself, due allowance must be made for this error in the standardisation of the solution. It is almost needless to remark that a similar precaution must be observed in taking the reading of the burette in the actual titration of the zinc solution of the ore. Results obtained were as follows:—

No.	5..	15.08	per cent.	zinc.
"	9..	23.80	"	"
"	11..	10.69	"	"
"	13..	6.85	"	"
"	20..	15.90	"	"

(To be continued).

CHESTNUT BARK TANNIN.*

By HENRY TRIMBLE.

In the manufacture of chestnut extract the bark and wood are used together, the latter naturally exceeding the former in amount as well as in yield of extract.

It has been thought desirable to determine if there exists any differences in the character of the tannins from these two parts of the tree, and the results of an investigation of that from the wood were published in the *Journal of the Franklin Institute*, cxxxii., p. 303.

The material in this case was obtained from a tree thirty years old, cut in August; the bark was immediately removed, air dried, and powdered.

The total tannin was found to be 7.31 per cent. The wood yielded 7.85 per cent. The other important con-

* Read at a Meeting of the Chemical Section of the Franklin Institute.

stituents in the bark were found to be in per cent, 1.09 of resin, 3.06 of mucilage, 1.35 of glucose, 10.00 of moisture, 4.71 of ash, and 45.44 of cellulose.

The tannin, as extracted by commercial ether, was much darker in colour than that similarly prepared from the wood, but an equally light coloured product was obtained by first precipitating in fractions with lead acetate, and then further treating the middle and most abundant one with salt and acetic ether. The aqueous solution of this portion, after removal of lead by hydrogen sulphide, when saturated with common salt, separated a dark coloured portion which rose to the top, and was easily removed in one mass after standing twenty-four hours. The remaining light coloured solution was agitated with acetic ether, the latter separated, and, after removal of the solvent under reduced pressure, a light coloured product was obtained. This was then dissolved in water, filtered, and the solvent distilled off under reduced pressure; it was then dissolved in ether, filtered, and again dried in a vacuum at the temperature of a boiling water-bath.

The product was a light, almost white, porous mass of a reddish brown shade, which was completely and readily soluble in water and the other usual solvents, and in all other respects corresponding with the chestnut wood tannin described in the previous paper, as well as with gallotannic acid. It did not give any reaction for glucose, from which compound it was rather more easily purified than the product from the wood.

The average of two closely agreeing combustions gave the following percentages, with which are given those from the tannin of the wood, for comparison.—

	Chestnut bark tannin.	Chestnut wood tannin.
C	52.42	52.11
H	4.67	4.40
O	42.91	43.49
	100.00	100.00

The conclusions to be drawn from this work are that the tannins from chestnut bark and wood are identical, and although ultimate analyses show high percentages of hydrogen in both, they are believed to be identical with gallo-tannic acid.

In an investigation of the darker tannin precipitated from aqueous solution by salt, the following percentages were obtained:—

C	55.18
H	4.72
O	40.10
	100.00

This product was considered to be a mixture of the tannin with its anhydride.

THE GOOCH CRUCIBLE.

By TH. PAUL.

THE author considers it useful to give as a supplement to the original memoir (CHEMICAL NEWS, xxxvii., 181) a process which has been for several years found satisfactory in Ostwald's laboratory at Leipzig.

These crucibles differ but little in shape from ordinary crucibles. They taper slightly downwards and have a flat bottom with narrow perforations, upon which there fits a removable sieve-plate. They were made at first only of platinum, but they are now to be had of porcelain in several sizes, and are very cheap. Platinum crucibles, in addition to the advantage of platinum apparatus in general, have the valuable property that the apertures in the bottom can be made very small and numerous.

Recently crucibles have been made according to G. C. Caldwell's design, which combine the advantages of both materials. The sides of the crucible are made of porcelain, but the removable bottom is of platinum. In order to preserve the porcelain crucibles, it is advisable not to expose them to the direct flame at once, but to heat them first upon a wire grating covered with asbestos paper, as they otherwise occasionally crack. In order to prepare the crucible for filtering, a cushion of prepared asbestos is placed at the bottom. This is effected by securing the crucible in a glass funnel by means of a very thin caoutchouc pipe, of corresponding width, connected with an aspirator tube. The asbestos (the preparation of which I describe below), is shaken up to a very thin pulp with much water in a small flask; this pulp, after the pump has been set in action, is poured into the crucible in a thin stream. After the water has run off, the bottom is covered with a uniform closely fitting layer of asbestos, which must be so thick that the apertures do not transmit light if the bottom is held up to the window. The perforated plate is then placed in the crucible, and a little water is poured through the filter (preferable from a flask, and not from the jet of a washing bottle, which disturbs the asbestos unnecessarily) until it runs off perfectly clear. Finally, it is gradually heated to incipient redness and weighed.

If the crucible is to be used for filtering, it is again connected with the funnel and the air-pump. The latter must be set in action before the liquid is poured into the funnel. The precipitates are washed as completely as possible by decantation. If the nature of the precipitate allows, very large quantities of water may be used, as it runs through the filter very quickly, and yet perfectly clear. The precipitate may be dried in the crucible, and at any desired temperature. Asbestos is particularly suitable as a filtering material, as it is not at all hygroscopic, and an asbestos filter dried at 100° weighs exactly as much as one heated to redness. Hence, and because when using the Gooch crucible no organic substance comes in contact with the substance, it is especially adapted for determinations in which ignition is either inadmissible or the burning paper may act upon the precipitate. This is the case with determinations of mercury, arsenic, silver, antimony, zinc, &c. Cobalt and nickel may also be very well determined in this manner; for these metals the circumstance is very important that the precipitates, after ignition, may be conveniently washed again. If the ignition has to be effected in an atmosphere of hydrogen, oxygen, carbon dioxide, &c., the lid of the crucible is simply perforated as in a Rose crucible.

In order to prevent the direct action of the gases of combustion, the crucible is placed in a larger one with a massive bottom. Still more convenient is a platinum plate with a high edge, in which the crucible is placed.

The asbestos is prepared by taking soft long asbestos and clipping it in short pieces with scissors. It is then boiled with strong pure hydrochloric acid, freed from all fine particles by washing on a sieve, and finally dried at the common temperature.—*Zeitschrift für Analytische Chemie*.

Existence of the Diamond in the Meteoric Iron of Cañon Diablo.—C. Friedel.—After the author's researches there can be no doubt as to the existence of diamond in meteoric iron. This is the first time that this precious stone has been found in what may be considered its primitive gangue. In all the rocks where it has been hitherto met with, even in the pegmatite of India, we may see that it has been introduced as such during the formation of the rock. Here, on the contrary, the very state of the diamond, which appears as a fine powder disseminated in certain parts of the meteoric iron, seems to indicate that it has taken its origin on the spot, and has been formed during the consolidation or the crystallisation of the mass.—*Comptes Rendus*, cxv., No. 24.

ON THE CATALYTIC ACTION OF ALUMINIUM CHLORIDE ON SILICIC ETHERS.*

By H. N. STOKES.

IF a little powdered anhydrous aluminium chloride be added to some ethyl trichlorsilicate, $\text{SiCl}_3(\text{OC}_2\text{H}_5)$, which is cooled by ice, it dissolves, but no reaction is observed; on removing from the ice bubbles of gas soon appear, and the reaction often becomes violent, attended by heating of the liquid. The gas, which burns with green edged flame and formation of hydrochloric acid, is obviously ethyl chloride. If now the liquid be gently heated it gradually becomes thick, then solid, and finally the entire amount of aluminium chloride sublimes unchanged.

If instead of trichlorsilicate, tetraethylsilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, be used, the reaction is in many respects the same, including the formation of ethyl chloride and the thickening of the liquid; but if the test-tube be connected with a condenser, it is seen that much ethylether is also produced. It may also be noticed that a relatively much greater amount of aluminium chloride than in the first case is required to produce the solid residue, while, unless a very considerable quantity has been added, none sublimes out on further heating.

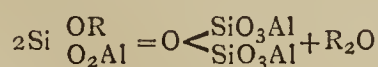
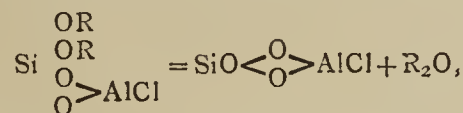
It will be shown below that the action of the aluminium chloride on the trichlorsilicate is a case of so-called *catalytic action* (this being defined as a change brought about by a substance which at the end remains unaltered), while its action on the tetraethyl ether is one which is purely proportional to the relative amounts of the reagents, the aluminium remaining finally in combination with silica. It will also be seen that the monochlorsilicate, $\text{SiCl}(\text{OC}_2\text{H}_5)_3$, is intermediate in its behaviour, a mere trace of aluminium chloride being sufficient to carry the decomposition to an end, when all the aluminium is found in fixed form. From these observations may be deduced the explanation of each case, including the catalytic action of the chloride on the trichlorsilicate. The details of the experiments, which were roughly quantitative, will be found in a separate section.

The only hypothesis which explains the facts observed is that in each case the substances react in a truly chemical sense, ethyl chloride and aluminium silicate compounds, $\text{Si}-\text{O}-\text{Al}$, being formed, but that in case of the chlorsilicates these bodies are exceedingly unstable, and decompose at once with regeneration of aluminium chloride, which is thus able to act again, and thus produce total decomposition when present even in traces.

The cause of this regeneration I take to be due, in part at least, to the tendency of the silicon to monopolise the oxygen, at the expense of the aluminium, forming $\text{Si}=\text{O}$, $\text{Si}-\text{O}-\text{Si}$, &c., whereby the metal is unable to remain combined with oxygen as long as this tendency of the silicon is not fully satisfied. If it happens that the latter is partly combined with chlorine (silicon chlorine), it at once exchanges it for an equivalent of oxygen. This, however, holds only in the aliphatic series of ethers, and in those cases where the chlorine is not the only constituent of the silicon compound. As I shall show elsewhere, silicon, when completely saturated with chlorine, as in silicon tetrachloride, does not show this tendency, neither does it exist in case of the aromatic silicates. From the latter, aluminium chloride, if in excess, takes all the oxygen, and the silicon becomes completely chlorinated.

The formation of *ethyl ether* I can explain only by assuming in silicon a well-known property of carbon, which is manifested in the ortho-ethers of carbonic and other organic acids, namely, that the highest basicity is shown only when all the basic radicals are organic, while the metallic salts are of a lower degree of saturation, and the mixed organic metallic ortho-salts are so unstable as

to be scarcely capable of existing under ordinary conditions. Assuming this analogy to exist, we should expect to find transformations like the following occurring:—



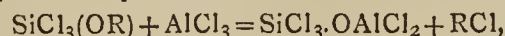
Strictly speaking, the tendency is not to form, as in the case of carbon, meta-compounds containing $\text{Si}=\text{O}$, the analogue of carbonyl, but groupings in which two silicon atoms are united by oxygen, $\text{Si}-\text{O}-\text{Si}$, or $(\text{SiO})_x$. This tendency is so strong, as has been pointed out by others (*i.e.*, Mendeleeff, *Grundlagen der Chemie, deutsch.*, Aufl. 767), that it is obviously the explanation of the fact that nearly all silicon compounds containing the analogue of carbonyl are not volatile, or volatile only at high temperatures, when by analogy with carbon the reactions producing them should give volatile bodies of low molecular weight. This tendency to condensation and polymerisation by means of oxygen is the rule in the silicon series, and forms one of the most marked differences in the chemical behaviour of these two elements, and the chief obstacle to producing by any simple means definite derivatives of silicic acid. I wish to be distinctly understood, therefore, as using the following formulæ and equations only as typical ones reduced to the simplest possible form, the actual ones being vastly more complex and of almost infinite variety. Where R is used it stands, for sake of simplicity, for ethyl. That the quantitative experimental results do not conform with absolute strictness to the theoretical explanation is not surprising, for aluminium chloride is an extremely reactive body, tending to produce all sorts of secondary changes, while it is not to be expected that the transformations could be carried quantitatively to an end by heating the viscous and finally solid masses which result.

Ethyl trichlorsilicate, $\text{SiCl}_3(\text{OR})$, is readily and completely decomposed by aluminium chloride, and the reaction is quite independent of the amount used, even a trace being sufficient. The products are ethyl chloride, free from ethyl ether, free aluminium chloride unchanged in amount, and finally a solid residue of the empirical composition $\text{SiO}.\text{Cl}_2$, but which in reality consists of a mixture of all sorts of complex silicon oxychlorides with free silica, the general result being expressed by the equation—

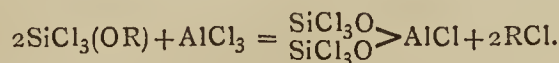


a typical case of catalytic action.

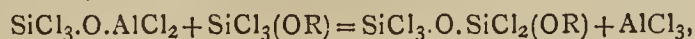
These oxychlorides are for the most part not volatile, by undergo at high temperature transformation into oxychlorides richer and those poorer in chlorine (Troost and Hautefeuille, *Ann. Chim. Phys.* [5], vii., 469), the result being that they lose weight on ignition. The reactions by which they can be formed in the present case are very numerous, and only a few typical ones are given. The first steps in the process are—



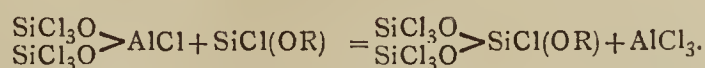
or—



These bodies, being for reasons above given very unstable, at once react with fresh portions of trichlorsilicate,—



and—



The regenerated aluminium chloride acts further, thus:—
 $\text{SiCl}_3.\text{O}.\text{SiCl}_2(\text{OR}) + \text{AlCl}_3 = \text{SiCl}_3.\text{O}.\text{SiCl}_2.\text{O}.\text{AlCl}_2 + \text{RCl},$

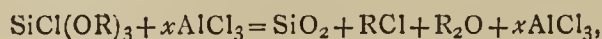
* From the *American Chemical Journal*, vol. xiv., No. 6.

which latter repeats the process, or may decompose, thus: $\text{SiCl}_3\text{O} \cdot \text{SiCl}_2\text{O} \cdot \text{AlCl}_2 = \text{SiCl}_3\text{O} \cdot \text{SiO} \cdot \text{Cl} + \text{AlCl}_3$, and so on in every possible way *ad infinitum*, the aluminium chloride being continually regenerated, while the tendency of silicon to such condensations leads to increasing size of the molecules, which tend to the limit $(\text{SiO} \cdot \text{Cl}_2)_x$, but seldom reach it before a high degree of complexity is attained. The increasing viscosity of the liquid interferes with the complete conversion of RO into RCl at a temperature below which other changes set in, which are manifested by more or less evolution of hydrochloric acid and gaseous hydrocarbons, with some carbonisation. There is, however, always an excess of silicon chlorine, which regenerates aluminium chloride, enabling it to act in minute amounts, and to reappear unchanged at the end.

It may be objected that these reactions are purely hypothetical, and that no such compounds as $\text{SiCl}_3\text{O} \cdot \text{AlCl}_2$ have been shown to exist. In the following cases it will be shown that there is strong evidence of their existence, the aluminium being caught in the act, so to speak, and found ultimately, not as chloride, but in combination with oxygen.

Ethyl monochlorosilicate, $\text{SiCl}(\text{OR})_3$.—Aluminium chloride, in acting on this compound, produces a similar series of changes, even if used in relatively small amount, with this difference, that as there is not enough silicon chlorine to carry the regeneration through to the end, the aluminium remains finally as Al_2O_3 , and probably also as AlCl , combined with silica. The process is also complicated in certain cases by the formation of ethyl ether, which was explained above.

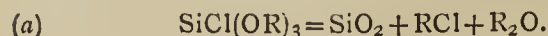
If we suppose the aluminium chloride to act by contact or influence merely, the decomposition would be expressed by the equation—



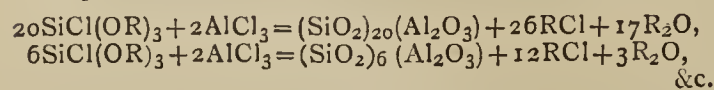
and the result would be practically independent of the amount of chloride used, which could be finally recovered unchanged. It is found, however, that while a mere trace is sufficient to bring about total decomposition in nearly the sense of the last equation, by increasing the amount more ethyl chloride and less ethyl ether are formed; when a certain proportion is reached, the ethyl ether vanishes, and also up to this point all aluminium remains fixed in the residue. If more than this amount of chloride be taken, some remains unchanged, and may be recovered by sublimation. We may consider three distinct cases, with differing proportions of the reagents, namely, when

$$\text{Si} : \text{Al} \begin{cases} > 3 : 2 & (1) \\ = 3 : 2 & (2) \\ < 3 : 2 & (3) \end{cases}.$$

The first case includes that where aluminium chloride is present only in traces, when the complete reaction, reduced to the simplest form and neglecting aluminium, would be—

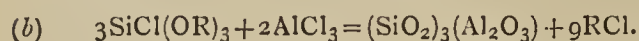


By increasing the proportion of chloride we have, for example,—



&c.

It will be noticed that the relative amount of R_2O decreases, and that of RCl increases as we approach the ratio $\text{Si} : \text{Al} = 3 : 2$. Reaching this point, which is case (2), we have—



The experiment shows that with this ratio no R_2O is formed, and that all aluminium remains in fixed form in the residue.

(To be continued).

NOTICES OF BOOKS.

The Coal-tar Colours. With especial Reference to their Injurious Qualities and the Restriction of their Use. A Sanitary and Medico-Legal Investigation. By THEODORE WEYL. With a Preface by Professor SELL. Translated, with permission of the Author, by H. HEFFMANN, M.D., Ph.D. Philadelphia: Blakiston, Son, and Co. London: Kegan Paul, Trench, Trübner, and Co., Limited.

A CAREFUL investigation of the physiological action of the coal-tar colours has now for some time been a desideratum. This want has been, generally speaking, supplied by the author. The information given is exceedingly valuable, though we may venture to express our regret that the terminology employed is not more in harmony with that current in Britain. It is apt to set our teeth on edge to find arsenic spoken of as "arsenicum," and magenta almost invariably as "fuchsin," or sometimes "fuschin." The word "noodles" will puzzle any English reader who is not versed in German. The ordinary English name for that preparation, which the Germans call "nudeln," is vermicelli. The English names for those styles in calico printing which the French name *reservage* and *enlevage* are respectively "resists" and "discharges."

The author shows that the dread of the coal-tar colours, so sweepingly and sensationally expressed in newspaper paragraphs, is exaggerated, and in many cases altogether groundless. A few of these colours, such as picric acid, dinitroresol, and Martius yellow, safranin, and methylene blue, are distinctly poisonous; whilst aurantia is, to say the least, doubtful. Magenta and the triphenylmethane colours generally are harmless if not contaminated with arsenic or mercury. Samples of these colours made by the old arsenical process are, of course, to be avoided, as are also such by-products as cerise.

Still, we must bear in mind that new coal-tar colours are being constantly invented and introduced into commerce, and that the confectioner and the wine merchant will employ such colours before chemists and physicians have had sufficient opportunity to decide on their composition and their physiological action. Our opinion is therefore in substantial agreement with the Austrian law, that the use of all the artificial colours ought to be prohibited in the preparation of foods and beverages. For such purposes, surely, the natural colours are amply sufficient. Dr. Weyl suggests, indeed, an international poison law for the whole of Europe.

From the abstracts of the legal enactments in force in different countries concerning the use of poisons in the preparation of foods and drinks, the British regulations are made to appear more efficient and more rational than is really the case. The penalty certainly must not exceed £50 for the first offence, but there is no minimum limit. Hence a sympathising magistrate may reduce the penalty to a mere nominal sum! Quite similar is the case with the "hard labour" for a term not exceeding six months. Would it ever be really inflicted?

Among the colours permitted in Austria-Hungary we find mention of "orlean," which is explained as "an infusion of yellow wood (probably fustic?) with one-fourth of alum and of gum." Orlean is generally used on the Continent to signify annatto!

Safflower is given as a permissible yellow colour. The flower certainly contains a yellow colouring matter, but it has little beauty.

The author's endeavours to find a relation between chemical constitution and physiological action are highly to be appreciated, and will, we hope, be successfully followed up.

Johnston's Catechism of Agricultural Chemistry. From the Edition [Dr. Sir CHARLES A. CAMERON. Revised and enlarged by C. M. AIKMAN, M.A., B.Sc., F.R.S.E., F.I.C., &c. Ninety-second thousand. Edinburgh and London: William Blackwood and Sons, 1892.

THIS work, so long and so justly a favourite, is in the present edition brought fairly up to the standard of our present knowledge of agricultural chemistry. It will be perceived that the authors, whilst fully recognising the value of lime in the form of gypsum on certain soils and for certain crops, are far from accepting the exaggerated importance ascribed to it by certain French authorities.

The question of the direct utilisation of atmospheric nitrogen by growing crops is not discussed here, being doubtless considered more suited for advanced students.

The use of ferrous sulphate as a dressing for land is here less favourably judged than it is by Dr. Griffiths. The view laid down in the present treatise agrees better with the general experience of farmers.

We find here no mention of the great advantage derived from the use of basic iron slags as an economical phosphatic manure.

The authors have—very judiciously in our opinion—retained the older and more familiar names for the chemical compounds used or met with in farming, to avoid perplexing the pupils. It is well pointed out that the object of this book is to teach, not chemistry, but scientific agriculture.

A System of Instruction in Qualitative Chemical Analysis. By A. H. ELLIOTT, Ph. D. New York: The Author.

THE author, it seems, "has found that chemical manipulation cannot be acquired by the reading of directions in a book alone." We were of opinion that this same conclusion had been reached long previously. Dr. Elliott proposes to train analysts in a very wholesale manner.

The instructor is to stand on a raised rostrum where he can be easily seen by every member of a class which may be one hundred in number! He is to perform the operations, and every student is to do the same at the same moment. We doubt if in case of nicer determinations this method is to be recommended.

As regards the subject matter of the book, we find them neither better nor worse than the instructions to be met with in other analytical manuals.

The Chemists' Legal Hand-book. By A BARRISTER, 1892. London: Offices of the *British and Colonial Druggist*.

THIS hand-book is designed solely for the information of the dealers in, and compounders of, medicines and poisons, known on the Continent as "apotheker" or "pharmaciens," but in England as "chemists." To the profession known abroad as "chemiker" or "chimistes," and in England devoid of any generally recognised name, it has little to say.

The author contents himself with explaining the law as it is without attempting to point out its many defects or to suggest their attending removal. Due mention is made of that most unhappy modification in the regulations for the preparation of methylated spirit, by which this article is rendered useless for the scientific investigator, without a series of red tape regulations.

A great hardship is also inflicted upon such persons—or would be if the law were carried out, as it may be any day—by the duty upon stills. The law is not limited to apparatus adapted for producing or rectifying excisable liquors, but seems to include every retort of whatever size, shape, or material. Nay, it almost appears to be by the mere grace of the Commissioners of Excise that scientific investigators "may keep and use stills for chemical experiments or for the manufacture of articles other than spirits or spirit-mix ures."

It even appears that persons who have applied for permission to buy methylated spirit free from mixed naphtha have been favoured with very annoying visits from the Excise.

It seems a farce to aim at the development of scientific chemistry and the improvement of our chemical manufactures so long as such barbarous regulations are kept up.

We ought to demand that the laws regarding stills shall be held no longer to apply to retorts, &c., made of glass, porcelain, stoneware, silver, or platinum, and that for such no license shall be required and no duty shall be chargeable. Further, the addition of a trace of Dippel's animal oil to methylated spirit should be introduced instead of mineral oils.

Elementary Chemical Analysis. By WILLIAM ACKROYD, F.I.C. Halifax: Whitley and Booth.

THIS little pamphlet contains nothing which can be pronounced erroneous or misleading. But, like nine-tenths of the elementary chemical treatises still showering from the press, we cannot see that it was required.

CORRESPONDENCE.

ANALYSIS VERSUS ASSAYING.

To the Editor of the Chemical News.

SIR,—The word analysis is used in many branches of knowledge with a meaning which is brought home to the student of chemistry when his teacher dwells on the difference between analysis and synthesis. It is a pity for a word of this kind to be degraded. In its passage from the lecture-room to the laboratory, however, it loses all precise meaning. The student is taught that analysis is an art of which only a few of the operations are analytical; he is taught to speak without blushing of the analysis of an element. He will learn to analyse sugar with a polariscope and copper with potassium cyanide. The analysis of a sample of butter can be made by determining its refractive index. Is it any wonder, then, that he comes to believe that whatever an analyst may choose to do is analysis, and that there is no use at all for the word assaying?

And yet this word assaying is a good English one, and has a vigorous existence. Long may it be so. And if the time must come when it will be used no longer, then may "trying" and "testing," which are its nearest representatives, be its successors.—I am, &c.,

J. J. BERINGER.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—If you will allow me to join in the discussion on the position of chemists I think I can give an explanation of why a chemist in many cases receives a low salary. To put it plainly, in the majority of instances he is not worth more than he gets. We chemists must not blind ourselves to the fact that our chemistry in itself is absolutely useless in most branches of commerce; it is the application of chemistry to commerce that is of infinite importance. We may compare chemistry to a foreign language in which invaluable facts are recorded; a man who is fully conversant with this language is of no value unless he can interpret it into "a tongue understood of the people." The chemist to whom a low salary is paid is one who is not yet an efficient interpreter; when he has perfected himself in this, his salary will rise; aye, and rise rapidly.

Is organisation (attractive delusive word) likely to force men, who know what they want, to pay men who can't give this to them large salaries? Would a Constantinople firm pay a Turk who could not express himself in English a large salary? No.

The remedy for low salaries is in the hands of individuals. Let the student fresh from college realise how useless he and his degrees are; let him take a low salary, keep his eyes and ears open and work; let him learn everything he can, whether it be engineering, stoking, German, or book-keeping; let him dirty his hands well, and in a few years, if the big salary does not come, he may rest assured that he is a duffer.

I speak from experience. Years ago, when I left college (highly recommended!), I was told by a large employer of chemists that I was only worth five shillings a week to him; and that was the salary he offered me. I did not believe him, and was mightily offended; but after seven months of looking for a berth, I accepted a low salary, and did some years' drudgery and knocking about in the world; to-day I see my salary growing from a respectable one to something better.—I am, &c.,

CAVEAT EMPTOR.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—I was very pleased to read the letters of "J. B. C." and "Dare Lucem" in reply to mine upon this subject; at the same time I am rather disappointed at the apparent apathetic disposition of chemical brethren generally, whose higher status is aimed at. If anything definite is to be accomplished it must result from general unison of action, for it cannot be expected that one or two willing hands shall build a golden bridge for others.

I clearly see the many difficulties to be contended with, but I do not think there are any insurmountable. As "Dare Lucem" aptly states, the time is gone for rule of thumb methods of manufacture, and practical science is absolutely necessary in order that successful combat may be made with the keen competition now existing. Rule of thumb must be ignored, and experience and practicality be recognised.

It is in our own hands to so formulate a scheme that employers will be pleased to know that they are able to rely upon the services of a chemist recommended to them with a certain amount of guarantee for his abilities and integrity, while chemists themselves will have protection and the dignity of the profession be maintained.

In "J. B. C.'s" letter he expresses a doubt as to the success of such a movement as is now suggested, because of those usurpers who are now so damaging to chemists of experience and ability. I should say that their admission into any such society should be most strenuously opposed, because the fundamental principle of such union of chemists must be that none but those who give positive proof of chemical training and specific practical knowledge shall become members.

If such things come to pass—and I fail to see why not—the usurpers, be what they may, will quickly become no factor in our problem.

I sincerely hope now that some chemists will communicate with me by letter (care of the office of this paper), so that we may at once take up the forming of some satisfactory scheme; and now the enhancement of the brilliant profession of a chemist is being promoted, let there be no apathy shown, but let one and all work with a determination to secure for ourselves what no Chemical Society has yet been able to do.

In conclusion, let me draw attention to the fact that a salary of £80 per annum is £1 10s. 9d. per week, and is practically the same sum as is now being paid to labourers for pulling down bricks and mortar at Millbank Prison. Here is food for reflection.—I am, &c.,

T. H. DAVIS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 24, December 12, 1892.

Description of a New Electric Furnace.—Henri Moissan.—(See CHEMICAL NEWS, vol. lxvi., p. 319).

Action of a High Temperature upon Metallic Oxides.—Henri Moissan.—This paper will be inserted in full.

Density of Carbon Monoxide and the Atomic Weight of Carbon.—A. Leduc.—The density in question is 0.96702; and the atomic weight of carbon = 11.913.

Critical Reduction of the Fundamental Determinations of Stas on Potassium Chlorate.—G. Hinrichs.—This paper requires the accompanying diagram. The author's final result is that all the atomic weights of Stas are inaccurate.

On a Carbon Chloriodide.—M. Besson.—The chief chemical characteristic of the chloriodide, $\text{C Cl}_3\text{I}$, is the ease with which it parts with iodine to form sesquichloride. In the action of aluminium iodide upon carbon chloride, C Cl_4 , there are formed other iodine substitution products, which the author has not isolated in a state of purity. They would be $\text{C Cl}_2\text{I}_2$ (a liquid), and C ClI_3 (a solid).

Action of Hydrofluoric Anhydride upon the Alcohols.—Maurice Meslans.—Below 130° hydrofluoric anhydride has no perceptible action upon absolute alcohol. Etherification is most conveniently effected at 220° .

Action of Sulphuric Acid upon Citrene.—G. Bouchardat and J. Lafont.—The portion of citrene not attacked by the acid is a saturated carbon, $\text{C}_{20}\text{H}_{22}$. It boils at 165 – 168° . The sulpho-conjugated acid, if saturated with baryta, yields barium sulphocyanate, $\text{C}_{20}\text{H}_{13}\text{BaS}_2\text{O}_6 + 3\text{H}_2\text{O}$, and a much more soluble salt, $\text{C}_{18}\text{H}_{14}\text{BaS}_2\text{O}_6 + 2\text{H}_2\text{O}_2$. A third salt is present in a quantity much too small for analysis.

Assay of Quinine Sulphate, and Determination of Quinine in Presence of the other Alkaloids of Chinchona.—L. Barthe.—This paper will be inserted in full.

Vol. cxv., No. 25, December 19, 1892.

This issue gives an account of the Annual Public Session, held on December 19th. It comprises the discourse of the President, M. d'Abbadie, in praise of deceased members and foreign associates of the Academy. Then follow the reports of the various commissions nominated to adjudicate on the memoirs presented in competition for the numerous prizes at the disposal of the Academy. Among the prizes offered for future research, we mention that founded by Dr. Jecker, *i.e.*, a sum of 10,000 francs, to be awarded each year for the most important discovery calculated to accelerate the progress of organic chemistry.

Journal für Praktische Chemie.
New Series, Vol. xlvii., Part 1.

On Hexamethylenamine. — L. Hartung. — The author has examined the action of benzoyl chloride and acetyl-chloride upon hexamethylenamine, the action of monochloroacetic ethyl ester, that of monochloroacetic ether upon hexamethylenamine in an alcoholic solution, the behaviour of inorganic acids upon hexamethylenamine, the action of sulphurous acid upon hexamethylenamine dissolved in benzene, the action of the same compound in isobutylic alcohol, in isopropylic alcohol, in methylic alcohol; the action of nitrous acid upon hexa-

methylenamine dissolved in glacial acetic acid, the decomposition of hexamethylenamine if boiled in aqueous hydrochloric acid, the decomposition of hexamethylenamine by nitric acid; hexamethylenamine and anilin.

The Oximes of the Fatty Aromatic Ketones, which in their Aromatic Residue contain the Halogen for Ketonic Combination in the Ortho-position.—Ad. Claus.—This paper does not admit of useful abstraction.

Origin of Phenyleneoxide.—W. Vaubel.—The author holds that the formation of resorcin from the para- or ortho-halogen phenols cannot be explained by Kekulé's scheme.

A Reply to H. C. Willgerodt.—F. Kehrmann.—A somewhat acrimonious controversy.

New Series, Vol. xlvi., Parts 3 and 4.

Researches from the Chemical Laboratory of Prof. Flawitzky at Kasan.—This paper discusses the connection between the forms of the oxygen and hydrogen compounds of the elements.

The Naphthenes, and their Derivatives in the Universal System of Organic Compounds (Part II.).—W. Markownikoff.—A voluminous memoir which does not admit of insertion.

Researches from the Laboratory of the University of Freiburg.—These comprise a paper by A. Claus on the quaternary ammonium bases of the quinoline series, and one by C. Willgerodt on the constitution of the nitrosoazo-compounds.

Researches from the Laboratory of A. Weddige.—This communication consists of a paper by M. Tschervan-Iwanoff on the preparation and properties of the polymeric di- and tri-chloracetonitril.

On some Xyloldisulphonic Acids.—Erik Pfaunenstill.—The author's results differ from those of Wischin in as far as on sulphonising the monosulphonic acids of metaxylol he obtains, not one, but two, disulphonic acids. He notices also briefly an ortho- and para-xyloldisulphonic acid.

Action of Zinc Powder and Alcohol upon Chloro-dibromhydrine.—G. Gustavson.—This paper does not admit of useful abridgment.

Correction to the Memoir "On Nitro- β -Naphtholes."—F. Gaess.—A correction of the diagrams in a paper to be found in this journal, vol. xlv., p. 614.

MISCELLANEOUS.

Royal Academy of Sciences of Turin.—The Ninth Bressa Prize.—The Royal Academy of Sciences of Turin, in accordance with the last will and testament of Dr. Cesare Alessandro Bressa, and in conformity with the Programme published December 7, 1876, announces that the term for competition for scientific works and discoveries made in the four previous years, 1889-92, to which only Italian authors and inventors were entitled, was closed on December 31, 1892. The Academy now gives notice that from January 1, 1891, the new term for competition for the ninth Bressa Prize has begun, to which, according to the testator's will, scientific men and inventors of all nations will be admitted. A prize will therefore be given to the scientific author or inventor, whatever be his nationality, who, during the years 1891-94, "according to the judgment of the Royal Academy of Sciences of Turin, shall have made the most important and useful discovery, or published the most valuable work on physical and experimental science, natural history, mathematics, chemistry, physiology and pathology, as well as geology, history, geography, and statistics."

The term will be closed at the end of December, 1894. The sum fixed for the prize, deducting the income-tax, will be of 10,416 francs. The person who intends to concur at the competition must declare it within the time above mentioned by means of a letter addressed to the President of the Academy, and send the work with which he concurs. The work must be printed; manuscripts are considered as nothing. The works of the concurrents which do not obtain the prize will be returned to them when asked for within six months from the adjudication of the prize. None of the national members, resident or not resident, of the Turin Academy can obtain the prize. The Academy gives the prize to the scientific man considered most worthy of it, even if he has not presented himself at the concourse.—M. LESSONA, The President of the Academy; A. NACCARI, The Secretary of the Commission.—Turin, January 1, 1893.

MEETINGS FOR THE WEEK.

- MONDAY, 9th.—Society of Chemical Industry, 8. "Qualitative Analysis of Colouring Matters," by A. G. Green.
"The Proportion of Free Fatty Acids in Oil Cakes," by Dr. B. Dyer. "Further Notes on Nitrous Oxide," by Watson Smith.
Medical, 8.30.
- TUESDAY, 10th.—Institute of Civil Engineers 8.
Royal Medical and Chirurgical, 8.30.
Photographic, 8.
- WEDNESDAY, 11th.—Society of Arts, 7. The Curiosities of Bird Life," by R. Bowdler Sharpe, LL.D.
Geological 8.
- THURSDAY, 12th.—Society of Arts, 4.30. "Upper Burma under British Rule," by H. Thirkell White, C.I.E.
Institute of Electrical Engineers, 8.
Mathematical, 8.
- FRIDAY, 13th.—Physical Society, 5. "On Science Teaching," by F. W. Sanderson, M.A.
Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.
Astronomical, 8.

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ST. PAUL'S SCHOOL, West Kensington.—An Examination for filling up about four Vacancies on the Foundation will be held on the 18th January next.—For information apply to the Bursar, St. Paul's School, West Kensington.

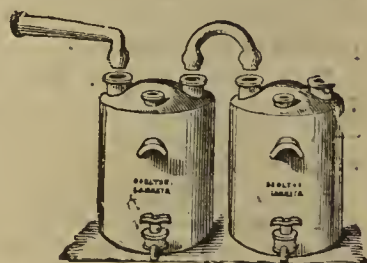
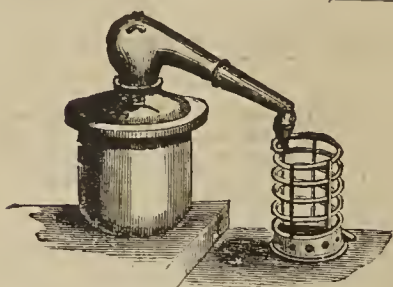
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THE CHEMICAL NEWS.

VOL. LXVII., No. 1729.

DETERMINATION OF IMPURITIES IN METHYLENES.

By ER. BARILLOT.

It is very important to ascertain in the industrial methylenes intended either for the methylation of aniline, or for the denaturation of industrial alcohols, the proportion of impurities, other than acetone, which these methylenes contain. The following method yields good results:—

Principle.—1. On agitating 20 c.c. of chloroform with a mixture formed of 10 c.c. of methylic alcohol, 15 c.c. sodium bisulphite of sp. gr. 1.325, and 5 c.c. of water, the coefficient of separation between the two non-miscible liquids is such that the chloroformic stratum preserves its entire volume if the methylic alcohol contains no other impurities than acetone. 2. If the methylic alcohol contains impurities (benzols, methylol, diallyl, &c.), the chloroformic stratum increases in proportion to their quantity.

Application.—1. Into a tube, *a*, of about the capacity of 40 c.c., we pour 10 c.c. of the methylene in question, then 15 c.c. of the solution of sodium bisulphite, stopper the tube, and shake it strongly. We add then 5 c.c. of water, shake up afresh, and allow the mixture to resume the ordinary temperature. 2. A glass tube of the capacity of 10 c.c., terminating below in a cock, communicates at its top by a narrower tube graduated in c.c.'s and tenths of a c.c., with a glass globe, *b*, holding about 200 c.c., the upper tubulure of which can be closed with a ground glass stopper.

Into this apparatus, *b*, we pour chloroform so as to fill the lower tube, the capacity of which is exactly 20 c.c. The meniscus of this liquid is then exactly level with the zero of the graduation into c.c. and tenths of a c.c. at the temperature 15°.

The mixture in *a* is poured into the apparatus *b*; we shake strongly, so as to obtain an emulsion of milky appearance and allow it to settle.

When the two liquid strata of the apparatus *b* are quite clear, we read off at 15° the increase of the volume of chloroform. This increase, multiplied by ten, corresponds to the percentage of impurities, other than acetone, contained in the methylene.

The alcoholometric of the methylene examined may be comprised between 80° and 99°. The proportion of acetone, from 1 to 30 per cent, does not affect the accuracy of the determination.

Having isolated the impurities which accompany methylene, we have made up a great number of synthetic samples with pure methylic alcohol, pure acetone, and the isolated impurity in order to check the accuracy of the procedure.

The results obtained with the various types of synthetic commercial methylenes are:—

	Impurity per cent.
A { Methylic alcohol, chemically pure	0
A { Pure industrial methylic alcohols used for the methylation of aniline	1 to 2
B { Methylenes, pure Government types, with 20 per cent acetone	1 to 2
B { Methylenes, pure Government types, with 5 p.c. impurity and 2 p.c. acetone	5
C { Strong smelling methylenes, with 10 per cent impurity	10
C { Very strong smelling methylenes	15 to 20

With the type B the denaturation is illusory, whilst with the types C the denaturation of the industrial alcohols is real.

The examination of a great number of samples of the methylenes of commerce has shown that often the denaturising impurities do not exceed 2 to 5 per cent, and that the methylenes which really denaturise alcohol contain from 10 to 20 per cent of these impurities.

The examination of the chloroformic stratum enables us to determine the nature of the impurity.—*Comptes Rendus.*

SEPARATION OF MICRO-ORGANISMS BY CENTRIFUGAL ACTION.

By M. R. LEZÉ.

THE micro-organisms comprise chiefly in their constitution substances heavier than water; these are the albumenoid, cellulosic, and mineral substances, which are isolated by incineration. If the living organisms float in liquids such as wine, cider, or milk, the specific gravity of which borders closely upon unity, it is because they probably contain small quantities of gas, and the force which impels them to rise or sink in a liquid heavier or lighter than their protoplasmic substance is certainly very feeble, regard being had to the very small dimensions of these bodies in question.

But we may intensify this tendency to separation by submitting vessels containing fermentable liquids and organisms to rapid rotatory movement. We have the centrifugal force at command, and can render it several hundred times greater than the intensity of gravitation.

In the laboratory appliances which we employ, the radius and the speed are: in the "lactocrit" turned by hand, 9 c.m. and 3600 rotations; in the steam turbine (Burmeister's design), 20 c.m. and 4000 rotations.

In the former apparatus the recipients submitted to centrifugal force are small tubes, drawn out for a certain length in a conical form, and sealed before the lamp at the point. The second apparatus is continuous, and enables us to whiz indefinitely increasing quantities of the liquid in question.

Rotation clarifies fermenting liquids and determines the formation of a glutinous or gelatinous deposit, either at the points of the small tubes or upon the sides of the turbine. On examining these muddy deposits under the microscope, we perceive that they consist chiefly of a heap of living organisms.

By this method we have separated the organisms from a considerable number of liquids in course of fermentation by submitting to the centrifugal zone musts in course of fermentation, decoction of hay, milk or its serum, after the separation of the cream or of the curd, saccharine liquids loaded with moulds, wines in acetic fermentation, &c. The organisms appear to separate the more easily the larger are their dimensions. We can very distinctly isolate the mycelium and the spores of mould and the saccharomyces, whilst bacteria are only imperfectly separated.

In one of the experiments we passed fermenting cider. The liquid was turbid, but it became perfectly limpid. Samples collected in open or sterilised bottles, and kept in the stove at 30° all became turbid the next day, and swarmed with bacteria. Yeasts were no longer found, and the alcoholic fermentation had disappeared.

In order to facilitate the separation we may either heat the liquid or add liquids lighter than water, such as ammonia or alcohol. This separation of bacteria may find an application in bacteriological research. In industrial practice we may, perhaps, by means of centrifugal force free polluted or insalubrious waters from the greater part of the organisms present, being careful to admit into the turbine no air but such as has been filtered through a thick layer of cotton.—*Comptes Rendus.*

THE DECOMPOSITION OF TIN SLAGS BY
THE FLUORIDE METHOD.

By H. N. WARREN, Research Analyst.

THE decomposition of siliceous slags containing the oxides of tin and antimony was, up to a comparatively recent date, brought about entirely by fusing the same with a mixture of carbonate of sodium and potassium; the tediousness and prolongation of the operation, however, induced the author to use borax as a fluxing agent in admixture with the carbonates. And so rapid and complete was the decomposition of these refractory substances that the operation soon became employed in most of the leading laboratories throughout the kingdom. A more accurate method, however, is still in readiness, oxides of tin and antimony having lately been proved to be by no means fixed when subjected to high temperatures in contact with alkalis; and in numerous instances the fumes collected by volatilisation from the crucibles containing these substances were found on examination to retain notable percentages of both tin and antimony; the nickel vessels employed are also liable to introduce further errors.

In employing the fluoride method, a convenient portion of the slag in a fine state of division is introduced into a platinum dish of suitable dimensions, and acted upon by an equal portion of hydrofluoric and hydrochloric acids, a gentle heat from a sand-bath being applied for a few moments. The slag almost immediately passes into solution, the solution thus obtained is diluted to a known volume, one-half being precipitated by the addition of SH_2 . The precipitated sulphides of tin and antimony thus obtained, after purifying if necessary by re-solution, are ignited and weighed as oxides.

The second half having been rendered alkaline by means of ammonia, a large excess of oxalic acid is added in order to re-dissolve the precipitate, the introduction of SH_2 in excess being maintained as before. Antimony sulphide alone falls, which is ignited and weighed as oxide. From the previous weight of the mixed oxides the percentage of antimony is at once obtainable by subtracting the latter.

By this method a complete separation and estimation of both metals can be performed in less than an hour, over three hundred samples of a like nature having been worked by this method during the past year to an accuracy of decimal 2 per cent.

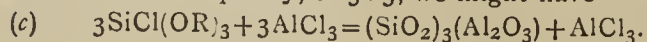
Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

ON THE CATALYTIC ACTION OF ALUMINIUM
CHLORIDE ON SILICIC ETHERS.*

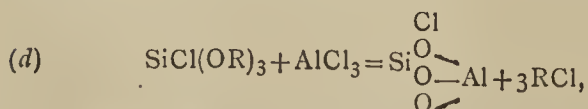
By H. N. STOKES.

(Continued from p. 10).

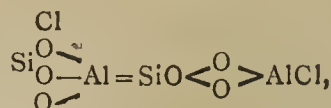
ANY further increase in the proportion of chloride belongs under case (3), where $\text{Si} : \text{Al} < 3 : 2$. For example, if the ratio be that of equality, or $3 : 3$, we might have—



In fact, when this proportion is taken, unchanged aluminium chloride sublimes out of the residue. Owing, however, to the tendency of the silicon to monopolise the oxygen or to take the metasilicate form, this proportion admits of another reaction:—



and



the residue being a chloraluminium metasilicate, or at least some similar form in which the preference of silicon for oxygen before chlorine is satisfied. The chlorine and aluminium in this form are practically fixed, as such a body as this would probably give off aluminium chloride, if at all, only at a high temperature, the effect being that the volatile chloride falls below the theoretical amount required by equation (c).

Finally, if $\text{Si} : \text{Al} = 1 : 2$ —



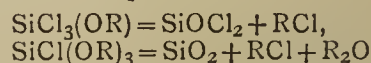
If we write the formula of the product—



it appears that in this form also the aluminium might be fixed, but that if more chloride be present, leading to the formation of $\text{SiCl}(\text{OAlCl}_2)_3$, such a body would, by virtue of the silicon chlorine present, decompose at once into AlCl_3 and $\text{SiO}(\text{OAlCl}_2)_2$. Two atoms aluminium are therefore the most that can possibly be held by one atom silicon reacting as monochlorsilicate; any further amount must remain finally as unchanged chloride. The stability of such bodies as $\text{SiO}(\text{OAlCl}_2)_2$ is, however, made improbable by the experiments, which show that even with the ratio $1 : 1$ only a part of the aluminium remains fixed.

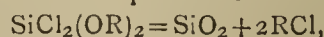
These equations do not explain the semi-catalytic action of aluminium chloride in decomposing indefinitely large amounts of monochlorsilicate. The reason is obvious when we consider that, as the experiments show, the greatest amount of aluminium which can be held fixed by 1 mol. wt. monochlorsilicate, lies between $\frac{2}{3}$ and 1 at. wt. (equations *b* and *d*). Any greater amount of monochlorsilicate will, by virtue of its silicon chlorine, regenerate aluminium chloride, and be destroyed thereby, until the above proportion is reached. At this point further reaction results only in the sense of *b* and *d*, the regeneration of the chloride ceases, and all aluminium remains fixed.

It will be observed that in these reactions the chlorine going to form ethyl chloride comes proximately from the aluminium chloride, but ultimately in part from the chlorsilicate, and that the equations—



are not strictly true, the aluminium acting as the agent by which Cl is transferred from Si to R. The hypothesis might perhaps be further tested by substituting aluminium bromide for the chloride. If the decomposition is due to influence only, $\text{SiCl}_3(\text{OR})$ should give SiOCl_2 , and RCl , and AlBr_3 only, but on the above hypothesis $\text{SiO} \cdot \text{Cl}_2$ with either RBr and AlCl_3 only, or a mixture of RCl , RBr , AlCl_3 , and aluminium chlorobromides, according to the proportions and the nature of the intermediate products. As this would involve previously studying the question whether a direct interchange of chlorine and bromine might occur, the experiment was postponed.

Ethyl dichlorsilicate, $\text{SiCl}_2(\text{OR})_2$, from similar considerations, should decompose thus—



and it is not possible to devise any probable reaction by which aluminium should remain permanently combined. Therefore the apparent catalytic action should be as obvious here as in the case of the trichlorsilicate. The experiments were, however, defective, probably owing to impure material, and no satisfactory conclusion could be drawn from them.

Ethyl orthosilicate, $\text{Si}(\text{OR})_4$.—This body shows a radically different behaviour from that of the chlorsilicates,

* From the American Chemical Journal, vol. xiv., No. 6.

the decomposition being strictly proportional to the relative amount of aluminium chloride used, and in this lies the explanation of the whole series of observations.

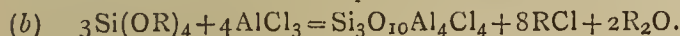
We may consider the following cases:—

$$\text{Si} : \text{Al} \begin{cases} < 3 : 4 \text{ (1)} \\ = 3 : 4 \text{ (2)} \\ > 3 : 4 \text{ (3)} \end{cases}$$

the ratio 3 : 4 being that in which the aluminium chloride contains just enough chlorine to convert all ethyl into ethyl chloride.

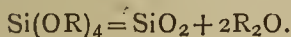


From considerations mentioned while speaking of the monochlorosilicate, it is obvious that this proportion may result in a certain amount of chlorine remaining combined with the aluminium up to the limit—



For practical reasons given below, the substances could not be made to react in this proportion, the result being a formation of ethyl ether, ethyl chloride, and sublimation of some unchanged aluminium chloride. For the same reason a reaction in the sense of case (1) was practically not to be brought about.

If the reaction were in any sense catalytic, it would follow that by reducing the aluminium chloride below the proportion $\text{Si} : \text{Al} = 3 : 4$, the decomposition would still be complete, but the amount of ethyl ether would increase relatively, while that of ethyl chloride would decrease, the limit being, with a trace of aluminium chloride—

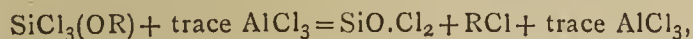


The actual result was that while with $\text{Si} : \text{Al} = 3 : 1$ the decomposition was complete, and approximately in the sense—

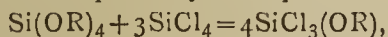


the slightest diminution of the amount of chloride below this ratio was followed by some of the silicate remaining totally unchanged. With $\text{Si} : \text{Al} = 3 : 0.9$, for instance, it was possible to recover some of it, and with $\text{Si} : \text{Al} = 150 : 1$ the merest trace of decomposition was discernible. This proportion in the case of the monochlorosilicate resulted easily in total decomposition. The only possible explanation of this difference is that in the case of the chlorosilicates the apparent contact action is due to constant regeneration of aluminium chloride by silicon chloride. The tetraethyl ether contains no silicon chlorine, aluminium chloride is not regenerated, and therefore acts only in proportion to the amount originally taken.

An experiment was made which shows the peculiar stability of silicon tetrachloride as compared with the chlorosilicates. It was supposed that since



by adding to tetraethyl silicate some silicon tetrachloride in the proportion required by the equation—



the chlorine of the tetrachloride would regenerate aluminium chloride, with the final result that solid silicon oxychloride and ethyl chloride would be formed. With even $\text{Si} : \text{Al} = 5 : 1$, and in sealed tubes at 100° , no solid was formed. Only after heating at 170° , at which temperature the tetrachloride acts on the ether, did total decomposition occur.

Anhydrous ferric chloride acts on both the tetraethyl silicate and the trichlorosilicate, but with much greater difficulty than aluminium chloride. Only at near the boiling-point (105°) of the trichlorosilicate was any marked reaction, with formation of ethylchloride, visible. The tetraethyl silicate reacted easily on heating, giving off ethyl ether and ethyl chloride and leaving a solid residue. The reactions were not further studied.

Anhydrous zinc chloride is without action on the tetraethyl silicate at its boiling-point (165°).

(To be continued.)

REPORT ON THE TECHNICAL DETERMINATION OF ZINC.*

(Concluded from p. 7).

Method of Mr. Mann Page, Chemist Omaha and Grant Smelting Company, Denver, Colorado.—The ore is decomposed by boiling in a casserole with a mixture of concentrated hydrochloric, nitric, and sulphuric acids, added separately in the order given, the amounts of acid varying according to the demands of the character of the ore under treatment to ensure complete decomposition. The boiling is continued until the fumes of sulphuric acid appear distinctly.

The casserole is then removed from the hot plate, contents allowed to cool, and the sulphuric acid solution diluted with water to three or four times its bulk, and chlorate of potassium added whether manganese be present or not.

If manganese is present, the chlorate must be added in quantity sufficient to ensure complete precipitation, an additional quantity of this reagent being added during the boiling if it appears necessary. This can be easily determined by the appearance of the solution. The precipitated manganese dioxide and the insoluble residue are now filtered off and well washed with boiling water.

To the filtrate ammonia water is added *in slight excess*, the precipitate well stirred, and immediately filtered off, the filtrate passing into a graduated flask of 250 c.c. capacity.

After the iron and alumina precipitate has been transferred to the filter—which should be a sufficiently capacious one—it is allowed to drain thoroughly, and then washed three or four times with water which has been rendered distinctly ammoniacal, and which should not be more than tolerably warm. In washing the precipitate care should be taken to thoroughly disintegrate it by the stream of wash water.

After a thorough washing, the filtrate is acidified by hydrochloric acid, the flask filled to the mark, its contents well mixed, and a number of aliquot portions of the solution taken from the zinc determination, which is accomplished by a standardised solution of ferrocyanide of potassium, acetate of uranium being used as indicator.

If copper be present, it must be removed previous to titration by means of granulated lead. The titration is always made in hot solutions.

Results were as follows:—

No. 5..	14.62	per cent zinc.
" 9..	22.00	" "
" 11..	10.50	" "
" 13..	6.30	" "
" 20..	15.37	" "

Notes on the above method:—

Attention has been called to the advisability of washing the iron precipitate with water which is not more than tolerably warm, it having been the writer's experience that a partial precipitation of the hydrated oxide of zinc takes place more easily from solutions which, while yet distinctly ammoniacal, approach more nearly the boiling temperature. The precipitation of the hydrated zinc oxide is furthermore influenced by the precipitation of the hydrated sesquioxide of iron, especially so when the solutions are very hot.

To prevent this occurrence the precautions previously indicated must be observed, in addition to which, as a further safe-guard, wash water, which has been rendered ammoniacal, or has been impregnated with chloride of ammonium is used.

Method of Mr. F. Mentzel, Superintendent San Juan Smelting and Mining Company, Durango, Colorado.—The method about to be described is based on the principle that in an almost neutral solution of sulphates or chlorides, the separation of zinc from iron, manganese,

* A report read at a meeting of the Colorado Scientific Society. From the *Journal of Analytical and Applied Chemistry*, vi., No. 9.

cobalt, and nickel can practically be effected by means of hydrogen sulphide, while if the solution contains about one-tenth of its volume of sulphuric acid the separation of zinc from copper is equally complete, provided the solution is heated almost to the boiling point before the precipitated sulphides are filtered off.

The *modus operandi* is as follows:—

One grm. of ore is decomposed in an eight ounce flask with 5 c.c. conc. hydrochloric and 5 c.c. conc. nitric acid; after the red fumes have ceased to be evolved, 5 c.c. conc. sulphuric acid are added, and the whole evaporated until the fumes of sulphuric acid appear. It is absolutely essential at this point that all traces of nitric acid should have been expelled, as otherwise correct results will be vitiated.

On the appearance of the sulphuric acid fumes the flask is removed from the hot plate, allowed to cool, about 50 c.c. water added, and a brisk current of hydrogen sulphide passed through the solution. In a few minutes the precipitation of the copper, &c., will have taken place. The precipitation is complete when precipitated sulphides are seen to settle rapidly at the bottom of the flask.

Now heat the solution as rapidly as possible almost to the boiling point, by which most of the absorbed sulphuretted acid will be expelled; any zinc which may have been precipitated will by this means be re-dissolved. Filter into a sixteen ounce flask, wash the precipitate with cold water three or four times, allowing the filter to run dry each time before renewing the wash water.

After washing, neutralise the filtrate with ammonia water, care being taken not to let the ammonia run down the sides of the flask, but to drop it directly into the liquid, the solution being constantly agitated while being neutralised. It is advisable to add a slight excess of ammonia, the ferrous hydrate precipitate being again re-dissolved by a few drops of dilute sulphuric acid (1:4). A slight permanent turbidity is of no consequence.

Now add an excess of four to six drops of dilute sulphuric acid, fill up the flask with water, and again introduce a brisk current of hydrogen sulphide into the solution. Within five to ten minutes a heavy sandy or powdery precipitate of whitish or yellowish zinc sulphide will appear, the rapid settling of which, and the clear supernatant liquid, being an indication of complete precipitation. The precipitate filters rapidly, and is indifferent to the influence of air, either during filtering or washing. It is filtered off and thoroughly washed, about five washings being usually sufficient unless the solution contained much iron.

The zinc sulphide which has adhered to the flask and the glass tube is now dissolved in 3 to 5 c.c. of hydrochloric acid, the solution diluted with an equal amount of water, and then poured on the filter containing the precipitate, which should immediately thereafter be covered with a watch glass. The greater part of the precipitate dissolves easily, the solution of any undissolved portion being effected with a few drops of conc. hydrochloric acid.

The bulk of free acid in the solution is now neutralised with ammonia water, and the zinc determined by titrating with standardised solution of ferrocyanide of potassium, using acetate of uranium as an indicator.

The following are the results obtained:—

Per cent Zinc.

No. 9.	No. 11.	No. 13.	No. 20.
23.63	11.17	6.94	16.15
23.56	11.13	7.05	16.05
23.56	10.99	6.76	16.10
23.73	10.99	6.81	16.02

Average.. 23.62 11.07 6.89 16.08

Method of Dr. H. C. Hahn, Chemist Colorado Smelting Company, Pueblo, Colorado.—The following method is one in which the determination of manganese as well as zinc is effected in the same solution.

Five-tenths of a grm. of ore is treated in a porcelain casserole with 2 c.c. conc. nitric, 3 c.c. dilute sulphuric (1:2), and 6 c.c. conc. hydrochloric acids, evaporated to dryness, or until the fumes of sulphuric acid appear. The casserole is then removed from the hot plate and allowed to cool, when 20 c.c. water are added, and the solution heated to boiling for about one minute.

The contents of the casserole are now transferred to an eight ounce beaker, and the solution nearly neutralised with a saturated solution of carbonate of sodium. In case too much of the latter should have been used, acidify with a few drops of dilute sulphuric acid.

Now add to the solution an excess of basic carbonate or lead suspended in water, until after vigorous stirring the precipitated hydroxide of iron settles quickly to the bottom of the beaker, leaving the liquid clear.

The solution should measure now about 80 c.c. It is heated to boiling without previous filtration, and the manganese determined with a standardised solution of permanganate of potassium (4.86 grms. of potassium permanganate to a litre, whence 1 c.c. equals 0.50 per cent Mn).

After each addition of the permanganate the solution should be briskly stirred, as it facilitates the settling of the precipitate. Should the solution appear yellow or turbid, the stirring must be continued until it is clear. When the rose tint appears, indicating the complete precipitation of the manganese, a few grms. of chloride of ammonium and 5 c.c. ammonia water are added, and the solution is filtered without previous heating, the precipitate being washed with water containing about one-fifteenth of its bulk of strong ammonia water.

The precipitate is well washed, and to the filtrate, which should measure about 140 c.c., 12½ c.c. of hydrochloric acid are added. If copper is present, it is removed by means of granulated lead, after which the zinc is determined by titrating with a standardised solution of ferrocyanide of potassium, an uranium salt being used as indicator.

The manganese determination is quite exact, but the zinc determination not so good.

The results on samples of ore submitted are:—

Per cent Zinc.

No. 5.	No. 9.	No. 11.	No. 13.	No. 20.
14.38	22.95	8.58	5.24	13.40
14.22	23.11	9.20	5.64	12.84

Average.. 14.30 23.03 8.89 5.44 13.22

Per cent Manganese.

No. 5.	No. 9.	No. 11.	No. 13.	No. 20.
3.22	2.89	2.68	9.25	0.65
3.32	2.81	2.72	9.53	0.87

Average .. 3.27 2.85 2.70 9.39 0.76

NOTE.—The basic carbonate of lead used in the preceding method is prepared by adding to a hot solution of carbonate of sodium a hot solution of acetate of lead as long as a precipitate is formed, and washing the precipitate repeatedly by decantation until all sodium salts are removed.

Comparison of Results.

Analyst.	No. 5.	No. 9.	No. 11.	No. 13.	No. 20.
Eakins	14.64	24.11	10.71	6.31	16.09
Von Schulz and Low	15.31	24.34	10.76	6.42	16.14
Jones	15.39	24.53	10.83	6.58	16.46
Hawkins	15.66	24.23	11.88	8.73	15.86
Knight	15.08	23.80	10.69	6.85	15.90
Page.. ..	14.62	22.00	10.50	6.30	15.37
Mentzel	—	23.62	11.07	6.89	16.08
Hahn	14.30	23.03	8.89	5.44	13.22

A consideration of the above results leads to the conclusion that there are a number of the methods detailed that are satisfactorily adapted for the technical determination of zinc. All of the technical chemists employ the ferrocyanide solution for the final titration.

A method, however, like the one used by Mr Mentzel will hardly commend itself on account of the repeated use of hydrogen sulphide. The unique method of Dr. Hahn for the combined determination of manganese and zinc from one solution is open to the serious objection that the zinc results are uniformly low. With this difficulty obviated, the method would be a highly commendable one.

The governing factors which should influence the selection of any given method for general adoption in technical laboratories are without doubt the accuracy of the results that can be obtained by its use, together with the time involved in its execution. When it is borne in mind that the technical chemist is daily confronted with a large number of determinations that are to be made, and that not only are metallurgical calculations, but also treatment charges on ores dependent on his results, the desirability of having simple, quick, and correct analytical methods is made apparent.

Without at all disparaging the methods employed by Messrs. Page, Hawkins, and Knight, it seems to the committee that the method described by Messrs. von Schulz and Low approximates more nearly to the conditions prescribed than do any of the others. It will be noted that the results given by Messrs. von Schulz and Low are comparatively high only in their determinations on samples Nos. 5 and 9, and attention is directed to the fact that in both of these samples the presence of cadmium is noted by Mr. Eakins, sample No. 5 containing the larger quantity. It is to be regretted that Mr. Eakins did not furnish the exact amount of cadmium contained,* but his results on this element were not requested by the committee, at the time the ores were submitted to him for zinc analysis.

The committee feels that the ores on which the investigations were made were such as have subjected the methods employed in the determination of zinc to a severe test. It is also aware that any method which would commend itself for general introduction must not only be a satisfactory one in the hands of its originators, but that it must also be capable of yielding concordant results when operated by others. This can only be determined by a fair and impartial trial.

If the inducements pertaining to von Schulz and Low's zinc method seem sufficient to warrant other chemists in investigating its merits, the committee will be glad to aid such in furnishing requisite material; and it will no less be pleased to publish such criticism as may be offered, if weaknesses in the method which are not now apparent are thereby disclosed.

E. N. HAWKINS,
F. C. KNIGHT,
L. J. W. JONES,
HENRY E. WOOD,
F. GUITERMAN,

Committee.

ADDENDUM.—The following corrections from von Schulz and Low were received too late for insertion in the proper place:—After the word "solution," p. 6, col. 1, line 6 from bottom, add the following:—Owing to the fact that ores rich in sulphur occasionally react too violently by this treatment, it is best to vary the method in such cases by first adding 5 c.c. strong nitric acid to the ore, and heating in a covered casserole until the mass begins to become pasty, and then remove from the heat and add 20 c.c. of the chlorate solution and finish the evaporation as usual.

"Uranium acetate," p. 6, col. 1, line 35 from bottom, and col. 2, lines 19 and 26 from bottom, should read "uranium nitrate."

* Mr. Guiterman, the Secretary of the Society, writes that Mr. Eakins has found 0.60 per cent cadmium in No. 5, and 0.15 per cent in No. 9. These amounts deducted from the results of the other chemists will give a better comparison with Mr. Eakins' on the samples in which cadmium was present.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, December 13th, 1892.

Mr. W. CROOKES, F.R.S., Vice-President, in the Chair.

Stas Memorial Lecture.

IN opening the proceedings, the CHAIRMAN said:—"We are met to-night at an Extraordinary Meeting to do honour to the memory of one of the greatest chemists of this century, I might almost say one of the greatest chemists ever known to the world. This day is the first anniversary of his death, and it is a very happy thought on the part of the Council of the Chemical Society to hold a meeting on the occasion, in order that you may hear an account given of his labours. I had the very great advantage of being, I might say, a personal friend of Stas. I have been in his laboratory and seen his arrangements and apparatus, and there witnessed, among other things, a large mass of chloride of potassium, which took him years to prepare, with which he had made the most refined experiments, without detecting the slightest trace of sodium. I think that fact alone a most wonderful evidence of his marvellous skill."

Dr. ARMSTRONG said, before reading the paper, he desired to state that it was a matter of great regret that it was impossible for Professor Mallet to be present. The Society were none the less much indebted to him, not only for having done what was asked of him, but more particularly for the example he had set. Last year, when a discussion arose as to the steps to be taken to secure appropriate notices of their eminent deceased foreign members, Stas and Kopp, the suggestion was made that it would be very desirable to take advantage of these and similar opportunities, not merely to give accounts of the work that our foreign members had done, but inasmuch as the foreign members are always men of great distinction and, as a rule, moreover, men who have lived a considerable number of years after they have accomplished their life work, that such notices, should, as far as possible, take the form of critical monographs of the subjects with which they have principally dealt. It seemed that in this way the Society would be doing educational work of very considerable service to its Fellows and to chemists generally. The matter was presented to Professor Mallet in this light, and there could be no doubt that he had responded in the most liberal manner possible to the appeal made to him; moreover, it was he who had suggested that a special meeting should be held on the anniversary of Stas' death. The delivery that evening of the first memorial lecture, therefore, was a very important step in the Society's history. It had been arranged that the work of Kopp should be dealt with in a similar spirit by the Treasurer, Professor Thorpe, in February next, on the anniversary of Kopp's death. Furthermore, it was proposed—and he hoped that in May next the proposal would be carried into execution—that, in like manner, on the anniversary of his death, the work of Von Hofmann should be commemorated. At present the plan was not fully developed, but it was somewhat as follows:—In order to deal with the subject from an English point of view, as our German *confrères* in Berlin were also engaged in the preparation of a similar account, it was proposed that Lord Playfair, who was intimately associated in early days with chemical science in this country, should recount his recollections of the state of chemistry at and prior to the time of Hofmann's arrival in England; that Sir Fredk. Abel should follow with an account of the work done at the Royal College of Chemistry under Hofmann, compiling this with the assistance of the remaining friends and pupils of Hofmann; and that the rise and progress of the coal-tar colour industry and its connection with the Hofmann

school should be sketched by Dr. Perkin, who, he was glad to say, had consented to make his contribution to a large extent autobiographical. Whether it would be possible also to include in this memorial notice an analysis of the chief chemical work of Hofmann was not yet decided, this task being one of no slight difficulty and magnitude.

The following paper was read :—

81. "*Jean Servais Stas and the Measurement of the Relative Masses of the Atoms of the Chemical Elements.*"
By J. W. MALLET.

The story of the life of Stas is first briefly told, and reference is then made to his researches in other directions than that of his specially chosen investigation of atomic weights; in order to fairly consider the contributions to knowledge in this latter direction which we owe to Stas, Professor Mallet next notices the succession of fundamental ideas which have gradually led up to the question, What is the mass of an atom of a particular element? This historical survey is followed by a lengthy section on the early history of investigations as to the atomic weights of the elements up to the year 1820; after which, reference is made to the determinations carried out from the time of Berzelius to that of Stas, a list, in chronological order, of the various published investigations being given.

Stas's work is then considered, the nature of the several general questions of fundamental importance in regard to matter as studied by the chemist, which he endeavoured to settle, being pointed out. These general questions are as follows :—

1. Is the mass or weight of an atom of a given element an absolutely constant quantity, so that chemical analysis, properly conducted, must always produce, from each substance examined, strictly the same relative quantities of the same constituents separated?

2. Assuming that the atomic weights of the various elements are severally fixed and immutable, are they represented by numbers which are commensurable, *i.e.*, are the atomic weights of all the other elements integer multiples of that of hydrogen?

3. If we assume the atomic weights of the elements to have constant values and to be represented by commensurable numbers, does not this indicate that all or most of the elements are, in reality, compound forms of matter—that, in short, we are as much called on to believe in the unity and unlimited interconvertibility of matter as in the unity and interconvertibility of energy?

4. Do experiments with substances raised to extremely high temperatures justify the belief that the elements may be dissociated into simpler forms of matter?

The rigour with which Stas investigated the methods of analysis, and the requirements he discovered and applied with a degree of patience and skill never before used in chemical investigation having been somewhat fully referred to, attention is directed to the results arrived at in the course of his elaborate researches.

The titles of his memoirs are given, together with a very lengthy list of the works and papers of other authors dealing with atomic weight determinations.

Professor Mallet then discusses, at considerable length, the objects to be aimed at, and the methods to be pursued in future investigations.

1. Attention is directed to the fact that Stas himself expressed the earnest wish that some other chemist, of sufficiently well established scientific authority, would take the trouble to check, by repetition, some one, at least, of his fundamental results.

2. It is eminently desirable that the work which Stas did for a few of the elements be extended to the entire list of those known—to rare as well as to common elements.

3. Certain of the elements particularly call for a more searching and exact investigation of their atomic weights—tellurium is a prominent example; cobalt and mercury

are others; of these, the former may be expected to have a weight intermediate between those of iron and nickel.

4. It is desirable, then, in cases, such as that of iron, for example, in which the accepted value has been determined by study of a single change, should also be determined by other and independent methods.

5. It is eminently desirable that an attempt be made to directly determine the ratio between the atomic weight of hydrogen and that of each of the halogens, without in any way bringing in the atomic weight of oxygen.

6. The uncertainty as regards the elements of the yttrium group, and, in a less degree, those of the didymium group, requires clearing up.

7. It would be well to submit to experiment, by means as refined as those employed by Stas, the question of the absolute exactness of the well known law of "multiples."

8. Further enquiry into the close approach of so many atomic weights to the integer multiples called for by Prout's hypothesis is required.

9. It is necessary that the apparent periodic relationships among the elements should be discussed not merely, as heretofore, with the aid of roughly approximate atomic weights, but with exact weights, and, therefore, that more precise determinations of the numbers we would discuss should be made.

In the final section of the paper, the methods which it is desirable shall be pursued in the determination of atomic weights are discussed in detail, under the following heads :—

1. Selection of analytical or synthetical processes.

2. Use of pure materials.

3. Vigilance in regard to extraneous or accidental causes of error.

4. Choice as to the quantities of materials to be used.

5. Practical precautions as to accuracy in manipulation.

6. Precautions in regard to weighings.

7. Measurements by volume of liquids or gases.

8. Calculation of results.

9. Advantage to be derived from the application of greater working force and ampler means than can be commanded by private individuals to the determination of atomic weights. In this section, Professor Mallet advocates the establishment of a laboratory in which a small corps of competent chemists should be engaged solely in revising the whole list of atomic weights, with every precaution that could be devised to secure accuracy.

10. Final form of statement of results. In this section, it is argued at length that all atomic masses should be expressed in terms of the mass of the hydrogen atom taken as unity. The adoption of any other basis tends to confuse the consideration of any natural relations between these constants, as has been pointed out by Stas himself in reference to the hypothesis of Prout; numbers which, on the basis of $O=16$, come very near to integers, cease to do so when H is taken as unity, and O has its true value, as determined by experiment, assigned to it.

The paper will occupy fully 60 pages in the *Society's Transactions*.

The CHAIRMAN, in proposing that hearty and sincere thanks be given to Professor Mallet for his paper, said the suggestions he had made were most valuable, and it was to be hoped they would stimulate the younger chemists to carry out investigations such as he had referred to. He could not help feeling that Stas was more honoured among the English-speaking races than on the Continent. On the occasion of his lamented death, twelve months ago, the scientific societies of Belgium petitioned the Government to purchase his apparatus and some of his pure materials, and, as many of his works could not be purchased, either because they were out of print or had been published in an inaccessible form, that funds should be voted for the publication of a complete set of Stas's memoirs and papers. After a considerable delay, the answer of the Government was to the effect that the

schools were sufficiently supplied with apparatus and preparations. There was one memoir that Stas wrote that would be most valuable if it could be published, but he heard it was locked up in a Government Department. Stas was employed by the Government to investigate and determine the suitability of alloys of iron and other metals for the manufacture of heavy ordnance; his researches on the subject were most valuable, and he obtained some most important results; but hitherto all applications for permission to peruse his reports have been met with a refusal. If they could be made public, they would undoubtedly be of great value, both scientifically and practically.

Dr. RUSSELL said that about twenty-five years ago, when working on the atomic weights of nickel and cobalt, he had the pleasure of seeing Stas in London, who took a very considerable interest in this work; at that time he had met with certain difficulties in purifying nickel: Stas took considerable interest in the matter, and wrote out for him a paper of instructions recommending him to follow a certain course, and, only a month or so ago, he happened to come across this.

Professor DEWAR said that he was sure all must agree that one of the greatest services that could be rendered to the memory of Stas would be the complete publication of his memoirs. Resident as he had been in Belgium during a very interesting period of chemical history, he knew something of the support Stas gave to what, at the time, was a most revolutionary addition to chemical science. All present were aware that Kekulé was Professor in Ghent during many years, and the speaker was sure that he would be the first to acknowledge that it was largely owing to Stas's influence and assistance as an authority in Belgium, not only as a scientific man, but as a member of the highest social and political circles, that he was so splendidly supported by the Belgian Government. Furthermore, when the early memoirs of Körner, that are now classic, in which he suggested the position theory as an addition to the benzene or ring theory of Kekulé, were first submitted to the Belgian Academy, it was really Stas who secured their publication, and it was his encouragement of Körner's work that promoted the advent of the position theory in organic chemistry. To touch on the vast work of his life, and to attempt to criticise his researches, makes an ordinary observer feel exceedingly small. He always felt that, in comparison with modern work, a paper by Stas was an oasis of intellectual fruitfulness in a desert of arid vapid publication. We were all alike; we were all equally to blame; at home and abroad there was the same general tendency: the result being that our scientific literature is burdened by too many trivial, common-place productions, exhibiting no trace of any desire to cultivate originality or thoroughness. No chemist could read a paper by Stas without feeling himself an exceedingly small man. The noble inheritance left by Stas to chemists must live for ever, and it will always be a pleasure to any chemist wishing to cultivate his higher faculties, to read and study, and attempt to imitate his works.

Professor DEWAR then referred to the determinations of the atomic weight of manganese and of the molecular weight of triethylamine, which he had carried out in conjunction with Dr. Scott (*cf. Proc. Roy. Soc.*, 1883, 35, 44, 347). We were greatly indebted to Professor Mallet for the admirable *résumé* he had given, and for his friendly and critical remarks. He also, said Professor Dewar, was of opinion that the near approach in quite a number of the atomic weights to whole numbers is still a matter of very serious suggestive interest, and he proceeded to call attention to the results obtained on taking into account the values that the late Professor Dittmar found for the oxygen and hydrogen ratio, remarking that no man more competent to deal with this subject could be found, and that all must deeply deplore his loss while engaged in doing such splendid work on the very question under discussion. If we accepted Dittmar's number, which is

corroborated by nearly half a dozen separate researches, 15.87, as expressing the ratio between the atomic mass of oxygen and the atomic mass of hydrogen, it appeared that the best-determined atomic weights fall into two totally different categories; some that apparently could not possibly be regarded as multiples of that of hydrogen approaching nearer, while others, seemingly very near to, are now far from being multiples of the atomic weight of hydrogen. Thus, silver, taking the Dittmar ratio, would come out very nearly a whole number, viz., 107.046. The most recent determinations of copper would give the value 63.09. Tin would be within 0.1 of a unit. In the same way, antimony would be within 0.1. Iodine, however, would be out. Zinc, also, would be decidedly out. Beryllium would be nearly a whole number. Bromine would be 0.26 out. There could be no doubt that in the case of gold the number would be 195.61; while platinum would be 193.28, cerium 139.06, and boron 10.87, or near that. Professor Mallet made reference in his paper, he believed, to chlorine as an element which no one anticipated would come nearer a whole number than half a unit; but, as a matter of fact, chlorine now came within 0.2, viz., 35.16 of this element, and would fall into the class nearly approaching whole numbers. He noticed that Mallet had adopted the latest value of nitrogen. In his 1865 paper, the value 14.045 was given by Stas as the result of a very large number of determinations. Prof. Dewar said he believed the number 14.055 was deduced entirely from experiments on the synthesis of nitrate of silver. Stas was so conscientious that he altered the value from 14.045 in his later paper in 1875, he believed, because the weight of nitrate of silver obtained by synthesis before fusion differed very slightly from the weight after fusion, and he thought that it was not fair to depend on the weight after fusion, because there might be a slight loss of nitric acid. Consequently, in his later paper, he adopted 14.055, but that number is the result only of two determinations of the synthesis of nitrate of silver, whereas in 1865 there were ten or twelve different reactions from which the atomic weight of nitrogen was shown to be 14.045, not 14.055. This led him to remark that if we took the weight of ammonium as directly determined, which is probably as accurate a weight as any of Stas's numbers, viz., 18.076, and deducted 14.045 from it, the atomic weight of hydrogen relatively to 107.9 of silver or 16 of oxygen was 1.0077. That would give a ratio of the atomic weights of hydrogen to oxygen, transforming hydrogen to unity, of 1 to 15.88, so that Stas's determination of the weight of ammonium, deducting his own value for nitrogen, gives the ratio of the atomic weight of hydrogen to oxygen found by Dittmar, Rayleigh, and all the more recent investigators. He did not say this result is a coincidence; it must be due to the accuracy with which Stas determined the separate atomic weights. It was interesting to observe that the most recent density determinations gave both nitrogen and oxygen a little too high from the gravimetric point of view. Thus the determinations of Leduc make nitrogen and oxygen respectively 13.99 and 15.9, instead of 13.93 and 15.87; this was what we should expect if the oxygen, as we believe, be a little too dense, being nearer its critical point than hydrogen is, and the same applies to nitrogen. He could not help thinking the proposal made by Prof. Mallet, that the determination of atomic weights should be given to a Board, would not turn out quite satisfactory in practice. But there were many points all would wish to clear up, and it would be a noble piece of work for some one to follow out Stas's own work, namely, to repeat any one of his fundamental syntheses. It would require a man of the type of Dittmar to do such work, however. Dittmar had, in fact, attempted the re-determination of one of Stas's values, and it was very important that we should have an explanation of the difference between the two workers. Dittmar had found in the case of lithium a number something like 6.86, whereas Stas's value was 7.02. Dittmar's method

involved the analysis of lithium carbonate. He also determined the value of sodium by a similar method, and obtained absolutely the same value as Stas for sodium. What was the explanation of such a remarkable difference in the value found by the Stas method? In the case of cadmium, also, there was apparently a difference of half a unit between some of the determinations. What was the reason of these differences? He referred to such cases as these two of lithium and cadmium, but there were others, and the problem was to find out how it is that methods nearly equally accurate, but differing essentially, give such discordant results, the work being carried out with the accuracy nowadays attainable. Finally, he was very glad to have had the opportunity of expressing his grateful thanks for the kindness of Stas in the past, and of bearing testimony to the great service he had done to science.

Dr. SCOTT referred to the work on which he was engaged in connection with Lord Rayleigh, with the object of determining the densities of oxygen and hydrogen, he having undertaken the determination of the volume ratios. Latterly, he had prepared hydrogen by passing steam into sodium, condensing it in palladium, and had obtained oxygen from oxide of silver; the experiments were made with successive fractions of the two gases driven off from the solid materials, which were kept in vacuous chambers sealed on to the gas analysis apparatus. He had now succeeded in obtaining the oxygen and hydrogen so pure that from the first fraction to the last he could detect no difference between them in the last series of determinations; whereas on using the hydrogen directly prepared from sodium and steam, the ratio was 1 to 2.00243, that calculated on the whole of the hydrogen separated from the palladium was 2.00245. The last two figures he could hardly depend on.

Dr. BAILEY thought that the extraordinary care taken by Stas in preparing and examining his materials, and in studying the changes made use of in his atomic weight determinations, served perhaps more than anything else to impress the student of his works. Referring to his own work, he mentioned having noticed that materials which are generally regarded as stable and non-volatile may be carried off by steam when their solutions are slowly boiled. Was it not conceivable that potassium chloride might thus be carried off in quantity sufficient to influence an atomic weight determination? He next spoke of the difficulty of obtaining concordant results in determining chlorine in the compounds of platinum metals. How this arose he was not able to say, but other workers had met with similar difficulties.

In closing the discussion the CHAIRMAN expressed agreement with previous speakers that atomic weight determinations could not well be carried out by an organisation such as Professor Mallet had suggested.

NOTICES OF BOOKS.

The Microscope: Its Construction and Management. Including Technique, Photo-micrography, and the Past and Future of the Microscope. By HENRI VAN HEURCK, Professor of Botany and Director at the Antwerp Botanical Gardens; late President of the Belgian Microscopical Society, Hon. F.R.M.S. and New York M.S. English edition. Re-edited and augmented by the Author from the fourth French edition, and translated by WYNNE E. BAXTER, F.R.M.S., F.G.S. London: Crosby Lockwood and Son. New York: D. Van Nostrand Company, 1893. Large 8vo., pp. 382, with three Plates and upwards of 250 Illustrations.

STANDARD works on the microscope, its manipulation, and its application, are not too numerous in our litera-

ture, and without any disparagement to the writings of Dr. Beal, of Carpenter, and Quekett, we can give the present volume a most hearty welcome. It is written by a thoroughly competent authority, and is fully on a level with the most recent improvements both in the construction of the instrument and in its management.

After an introductory chapter on elementary optics we find an account of Prof. Abbe's theory of microscopical vision, and a series of experiments on the application of this theory due to Mr. J. W. Stephenson and laid before the Royal Microscopical Society of London by Mr. F. W. Stephenson.

In Book I., Chapter I., the author enters upon the microscope generally, passing on to a detailed examination of its parts. Here we regret to notice a defect of the book. The figures are duly lettered, but there follows no complete reference to the lettering, so that the figure is in some cases useless. Objectives and tests are very clearly described. Stages, movements, diaphragms, and condensers come next under review, the references to the lettering being still very deficient. This is particularly to be regretted in case of the Abbe condenser (Fig. 70).

Under accessory apparatus we have an account of the microspectroscopes of Sorby and Zeiss, the figures of the latter instrument lettered, indeed, but without explanation. As an illuminant, in default of daylight the author uses a petroleum lamp, or the electric glow-light, where available. Like all practical authorities he recommends that the windows of the work-room should face the north or the north-west. M. Van Heurck does not consider that microscopic research, if properly conducted, is injurious to the eyes. On this subject he gives some very judicious advice.

A very important part of the work is devoted to the compound microscopes of the best makers, the peculiarities of the various models being carefully described, and the instruments themselves are figured. In many cases there is a tabular account of the objectives furnished by the principal firms, giving the equivalent focus, the numerical aperture, and the price of each. It will be remarked that the production of apochromatic objectives is not now confined to the firm of Zeiss and Co., of Jena.

Among the makers Messrs. Powell and Lealand meet with high, and we believe fully merited, praise. It is said that their instruments are used in England by all "serious microscopists." This epithet is a gallicism which will call up a smile. Watson and Sons, who carry out certain specifications of the authors, are highly praised and have carried off high honours at the recent Micrographic Exhibition. The firm of Carl Zeiss, of Jena, is, however, characterised as the most important in the world.

Photo-micrography is expounded at great length in Book III., Chapter II.

A very important section treats of the cause of errors in microscopical observations, such as iridescence and diffraction, *Musca volitantes*, astigmatism, and dust on the glasses. After some useful remarks on the preservation of the glasses, the author proceeds to give instructions for preparing objects. In preference to Canada balsam he recommends storax and liquid amber, which have the advantage of not darkening on long preservation.

The arsenical medium of H. L. Smith, realgar, dissolved in arsenic bromide, the author obtains by melting together in a retort 1 part of sulphur and 1.7 part of arsenious acid heated to the distilling point. A caution is given concerning the dangerous vapours. In a subsequent formula 30 parts flower of sulphur are dissolved in 10 parts bromine, and the whole is heated with 13 parts of pure arsenic in fine powder, and heated until a drop taken out and cooled becomes very brittle.

An interesting chapter entitled "The Microscope in the Past and the Future," gives a history of this instrument and suggestions as to its future development. In

fine, Dr. Van Heurck's work must be pronounced a boon to all English readers interested in microscopy.

We regret that the translator has repeatedly used the term "Marie-bath" in place of the recognised and intelligible English word water-bath. "Bain-marie" is a survival of ignorance and superstition to which the French still cling, but there is no excuse for the attempt to introduce it in English writing.

The index is admirable, and the entire getting up of the book reflects the greatest credit on the publishers.

CORRESPONDENCE.

DISINFECTANTS—AN EXPLANATION.

To the Editor of the Chemical News.

SIR,—Dr. Klein's rejoinder calls for an answer. I have already shown that in his first letter (I mean the one in which periodate crystals were erroneously quoted with "aminol") certain statements were partly incorrect, partly misleading. I now confine myself to such matters as have not been touched upon in my previous letter.

I again quote from Dr. Klein's report: "This solution (1 in 600) is in itself a perfectly harmless fluid as regards the human organism; therefore, when applied to wounds, no undesirable disturbances could ensue owing to its being absorbed. This is well known to be the case with some antiseptics, as in carbolic acid applications, or in the use of perchloride of mercury."

And now I shall quote from "Koch, on Disinfection," abstracted and translated by Whitelegge, published by the New Sydenham Society.

(1) "For practical purposes a disinfectant should not require much longer than twenty-four hours."

(2) "Except chlorine, bromine, and iodine, only mercuric chloride, osmic acid, and potassic permanganate (5 per cent) destroyed anthrax spores within twenty-four hours. Since a 5 per cent solution of permanganate is inadmissible for disinfection in bulk, and osmic acid is out of the question, we have left only mercuric chloride and iodine, bromine, and chlorine."

The strength in which the above-named substances succeeded in destroying anthrax spores in twenty-four hours are stated in Koch's tables, thus:—

Permanganate aqueous solution	..	5 per cent (1 in 20)
Bromine	" "	.. 2 " (1 in 50)
Chlorine	" "	.. ?
Iodine	" "	.. ?
Mercuric chloride	" "	.. 1 " (1 in 100)
Osmic acid	" "	.. 1 " "

Now put against these declarations and records of Koch's the fact that Dr. Klein found "aminol" (strength 1 in 600), which he himself calls a perfectly harmless fluid, kills 94 per cent of the spores of anthrax in twenty-four hours, and its claim to be classed amongst true disinfectants is too obvious to be gainsaid.

That the designation "a true disinfectant" is meant by me to apply only to such strengths of solutions of "aminol" as have the power of destroying anthrax spores in twenty-four hours or thereabout, Dr. Klein may rest assured, as also that nothing has been or will be done by me intentionally to commit him to anything which is not fully warranted by his results as recorded in his authorised published report.—I am, &c.,

HUGO WOLLHEIM.

101, Leadenhall Street, London, E.C.,
January 4, 1893.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—The letters of your correspondents, Mr. T. H. Davies and "Dare Lucem," again open the question of the position of the Institute of Chemistry and of chemists in relation to it. It must be admitted that the Institute made no really satisfactory progress until within the last year or two, when signs of some sort of improvement were shown by the fact that the examinations were conducted upon approximately reasonable lines. The position of the Institute up to the present, in the opinion of a large section of its members, has been unsatisfactory for the reason that a constant majority of the Council has consisted of Fellows more interested in teaching than in the practice of Consulting and Analytical Chemistry, and it is evident that the proper step to take in order that progress may be made is to reverse this condition of things by electing as Members of Council a majority of Fellows who are Consulting and Analytical Chemists either in active general practice or in connection with Works, or who are concerned with special technical processes.

The knowledge and experience required by persons acting as Consulting and Analytical Chemists is very different from that required for teaching chemistry. It is well known that some lecturers and teachers do not appreciate the extent of that knowledge and experience required for the professional work referred to. It seems curious, therefore, that the Council of the Institute should be composed chiefly of those who do not belong to the class of members (by far the largest) for whose benefit the Institute was specially founded. The Institute of Chemistry Reform Association desires to obtain an alteration in this respect at the next election, and I would venture to suggest through your columns that chemists engaged in general practice, or who are more concerned with the duty of acting as advisers to the public or to private individuals than with that of teaching students, should endeavour to bring about the necessary change in the constitution of the Council.

We are perfectly cognisant of the valuable services to the Institute which have been rendered by many eminent professors of chemistry, and we have not the least desire to lose the advantage of their guidance and even in many respects of their control; but we feel sure that it is only reasonable to ask that the majority of those on the Council should consist of members for whose advantage the Institute was specially founded.

As a preliminary step we are suggesting the names of three Fellows of the Institute who are more interested in Consulting and Analytical Chemistry than in teaching for election as members of Council, and I shall be glad to supply forms to any member of the Institute who has not as yet signed a nomination form, and who may be willing to support any one of the three suggested candidates.—I am, &c.,

WILLIAM THOMSON,
Hon. Sec. to the Institute of Chemistry
Reform Association.

Royal Institution Laboratory Manchester,
January 5, 1893.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—In common, no doubt, with other Fellows of the Institute of Chemistry, I have this morning received a circular from a body calling itself the "Institute of Chemistry Reform Association," signed by Mr. Wm. Thomson, as hon. sec., in which I am asked to inform the Committee whether I will or will not support them in their endeavours to transform the minority of analytical chemists on the Council into a majority.

I shall be grateful if you will afford me space in which

to give my reasons for not thinking that such a change would be advantageous to the body of Fellows and Associates forming the Institute.

I take it that, as its name implies, the Institute is intended to exist for the benefit of all who are chemists and not of analytical chemists only, which seems to be admitted by the Committee of the Reform Association, as in their circular they "appreciate the valuable services rendered to the Institute by eminent professors of chemistry, and desire to retain many of them on the Council, but . . ." In fact, they think there are too many of them!

Now, sir, as one of the functions of the Council is to ascertain the fitness of those who present themselves as candidates for admission to the Institute, it is of vital importance that no action should be taken which would in any way have the effect of lowering the standard of admission. But this, I fear, would be the result of having a preponderance of analytical chemists upon the Council.

Without in the least implying that the three gentlemen for whom we are asked to vote are not fit and proper persons to be nominated, it is highly probable that a majority of analytical chemists would take a less broad view of the education necessary for membership than a majority of professors.

Analytical chemists tend to become specialists, and in the routine work of their profession there is little time for them to make themselves acquainted with the work done in other branches of knowledge, scientific or literary. Professors, on the other hand, have far better opportunities of knowing what is being done both in chemistry and in other subjects, for, in the former they are obliged in the course of their ordinary vocation to revise periodically their knowledge of the subject, and as to other subjects the nature of their work gives them more abundant leisure than any analytical chemist in good practice can have.

It is the practice in the laboratories of many analytical chemists to take pupils and to train them by giving them the ordinary analytical work of the laboratory to do. I will not dwell either upon the morality of sending results to clients which have been obtained by inexperienced pupils, nor upon the cutting down of fees by the employment of such pupils, although such action is the cause of the discontent at present existing in regard to the Institute. But if analytical chemists were to become a majority on the Council, there is little doubt that the first action taken would be to make the record of the work done by a candidate in an analytical laboratory a principal element in the admission examination. To those who know how, in too many cases, such pupils are suffered to pick up their knowledge, and who recognise the limited nature of the instruction to be obtained in the majority of professional laboratories, the prospect of such action is not re-assuring.

It is because I believe that if the Reform Association should carry its nominees, the value of the title of Fellow will become degraded, that I, a practising analytical chemist, decline to assist the Committee in their endeavour, and not because I have anything to say against their nominees personally.—I am, &c.,

R. W. ATKINSON.

Cardiff, January 10, 1893.

Royal Institution.—On Tuesday next (Jan. 17), Prof. Victor Horsley, F.R.S., will begin a course of ten lectures on "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology." On Thursday (Jan. 19), the Rev. Canon Ainger will begin a course of three lectures on "Tennyson," and on Saturday (Jan. 21), Dr. C. Hubert H. Parry will begin a course of four lectures on "Expression and Design in Music" (with Musical Illustrations). The Friday Evening Meetings will begin on Jan. 20, when Prof. Devar will give a discourse on "Liquid Atmospheric Air."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 24, December 12, 1892.

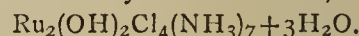
The Rise of Temperature under the Influence of Injections of Soluble Microbian Products.—MM. Bouchard and Charrin.—The authors discuss the increase of animal heat produced by the injection of microbial liquids, even if previously filtered.

Temperature of the Electric Arc.—J. Violle.—The author has experimented upon the electric arc as obtained under a great range of conditions. He finds that the hottest part of the positive carbon and of the arc has a temperature of 3500°, which is the heat at which carbon is volatilised.

The Magnetic Properties of Oxygen at Different Temperatures.—P. Curie.—This paper requires the two accompanying figures.

The Fusion of Calcium Carbonate.—A. Joannis.—The author is of opinion that calcium carbonate cannot be fused without the aid of extraneous pressure except at temperatures notably exceeding the melting-point of gold.

Ammoniacal Compounds derived from Ruthenium Sesquichloride.—A. Joly.—The limited action of water upon the ammoniacal chloride produces a liquid of an intense violet-red colour. If the anhydrous chloride in a state of fine division is projected into an ammoniacal solution saturated at a very low temperature and allowed to digest for some time, the deep red liquid obtained deposits small brown crystalline laminæ,—



The solution of this salt is red by transmitted, but violet by reflected light. Its tinctorial power is comparable to that of the most intense organic colouring-matters. A solution at 1:100000 transmits only the red and orange rays. A solution at 1:500000 is still of a distinct rose colour. If the solution is boiled it is rapidly destroyed, but it yields intermediate products, violet red, violet black, and, lastly, black.

A Phosphorus Iodosulphide.—L. Ouvrard.—This compound may be obtained by dissolving in carbon disulphide quantities of sulphur, phosphorus, and iodine, corresponding to the formula $\text{P}_2\text{S}_3\text{I}$. It forms brilliant crystals of a golden yellow, permanent in dry air, but slowly attacked by moist air with an escape of hydrogen sulphide. It is very soluble in carbon disulphide, sparingly soluble in benzene and chloroform, and still less soluble in ether and absolute alcohol.

Action of Bismuth upon Hydrochloric Acid.—A. Ditte and R. Metzner.—Like antimony, bismuth is not affected by hydrochloric acid if every trace of oxygen is excluded. If oxygen is present, a corresponding quantity of the metal is dissolved.

The Action of Potassa and Soda upon Antimony Oxide.—H. Cormimboeuf.—In the moist way, soda acting upon amorphous antimony oxide forms sesquibio- or tri-antimonites, whilst potassa produces a tri-antimonite alone.

The Relation between Formation-Heats and the Temperatures of the Point of Reaction.—Maurice Prud'homme.—For one and the same series of substances the formation-heat of the unit of mass is proportional to the specific heat, and inversely as the absolute temperature of the point of reaction.

Study of the Chemical Reactions in a Liquid Mass by the Index of Refraction.—C. Féry.—This memoir requires the accompanying diagram and table.

A Propylamidophenol and its Acetylic Derivatives.—P. Cazeneuve.—Propylamidophenol in an alkaline solution is a powerful photographic developing agent. According to M. Lumière, this power is found in aromatic substances, having at least two phenolic OH, or one NH₂ and one OH group, and that these two groupings must be in the *ortho*- or *para*-position. The *meta*-position yields only indifferent substances. Thus pure resorcline does not develop, whilst pyrocatechine and hydroquinone develop.

Determination of Impurities in Methylenes.—Er. Barillot.—(See p. 15).

Separation of Micro-organisms by Centrifugal Force.—R. Lezé.—(See p. 15).

Losses of Ammonia in Farm-yard Manure.—A. Muntz and A. Ch. Girard.—The observations of the authors show that the losses of ammonia chiefly take place in the stables, and that abundance of litter is no remedy.

The Fermentations of Dung.—Alex. Hébert.—The losses of nitrogen from farm-yard manure kept duly moist do not take place in the state of ammonia. Hence the addition of ferrous sulphate, of gypsum, or sulphuric acid is not of much use.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. vii. and viii., No. 23.

Utilisation of Burnt Pyrites for the Manufacture of Salts of Iron.—A. and P. Buisine.—The author treats the finely pulverised pyrites with sulphuric acid of from 50° to 66° B., using a temperature not exceeding 300°. At this heat the authors obtain a sulphate which is slightly basic, and which they propose as a substitute for ferrous sulphate, in agriculture, in the purification of coal-gas, as a disinfectant, &c.

Purification of Sewage with Ferric Sulphate.—A. and P. Buisine.—The authors show that it is possible in this manner to purify continuously large volumes of sewage. They consider that for this purpose it is superior to lime, which is self evident. They propose to extract the fatty matters from the precipitate by means of carbon disulphide, and to use the rest of the organic matter as a manure, which is said to contain 3 per cent of nitrogen.

Condensation of the Aldehyds of the Fatty Series with Cyanacetic Acid.—M. Fiquet.—Not adapted for useful abridgment.

Rotatory Power of Fibroine.—Leo Vignon.—The matter precipitated by alcohol from the hydrochloric solutions of fibroine is identical with fibroine. It possesses the same weight, the same action upon polarised light, and behaves in the same manner with reagents and colouring-matters.

New Preparation of Acetylene.—L. Maquenne.—Barium carbonate is the only one of the alkaline-earth compounds which is by degrees almost entirely transformed into a carbide under the influence of magnesium. Calcium carbonate is only very incompletely attacked, and gives then, if treated with water, a poorer mixture of hydrogen and of acetylene.

The Preparation of Ethylene Periodide (Tetraiodethene).—L. Maquenne.—The author obtains this compound by submitting acetylene to the action of iodine in an alkaline solution.

Action of Ammonia and the Amines of the Fatty Series upon Acetylacetone.—A. and C. Combes.—This extensive paper does not admit of useful abridgment.

The Pyrogallol Antimonites.—H. Causse and C. Bayard.—The authors describe the acid and the neutral compounds, and the behaviour of the latter with acetic anhydride and acetyl chloride.

The Action of Diamines upon Acetylacetone.—A. and C. Combes.—An extension of the former paper to the diamines.

Detection of the Radicle Benzoyl in Organic Compounds.—E. Leger.—For the detection of cocaine in toxicological analyses, Ferreira da Silva proposes a reaction characterised by the formation of odorous products easy to recognise. It consists in treating some m.grms. of cocaine, or of one of its salts, with fuming nitric acid at 1·4 specific gravity, evaporating to dryness in the water-bath and pouring upon the residue some drops of a concentrated alcoholic solution of potassa. There is then evolved a very distinct odour resembling that of peppermint. According to Béhal, the odoriferous principle is ethylbenzoate. M. Leger finds that the reaction is produced with other substances which, like cocaine, contain the radicle benzoyl.

The Preparation and Properties of Fibroine.—Leo Vignon.—The author takes a skein of clean white silk weighing about 10 grms., and treats it for thirty minutes at ebullition in a bath of 150 grms. neutral white soap and 1500 c.c. distilled water, turning it frequently. The silk is then wrung, rinsed with distilled water, first hot and then luke warm, to remove the soap. When drained it is submitted for twenty minutes to the action of a second boiling soap bath of the same composition as the former. It is then carefully drained, rinsed successively in 1 litre of boiling distilled water, 1 litre of luke-warm distilled water, 1 litre of cold distilled water containing 10 c.c. of pure hydrochloric acid at 22°. Lastly, it is again rinsed in distilled water and twice washed in alcohol at 90°. We thus obtain 75 per cent of silk very white, brilliant, supple, tenacious, and elastic, which must be regarded as true fibroine. Its specific gravity is 1·34. Its mean percentage composition is—

C	48·3
H	6·5
N	19·2
O	26·0
<hr/>	
	100·0

The ash of silk is about 0·80 per cent, but that of fibroine is only 0·1. If dissolved in concentrated hydrochloric acid, fibroine is strong lævorotatory, $\alpha_D = -40^\circ$.

No. 24.

The Rotatory Power of Cyclic Bodies.—Aibert Colson.—The product of asymmetry, based upon the theory of asymmetric carbon, cannot generally indicate the direction of the deflection in bodies possessing a rotatory power; and the theory of asymmetric carbon is an incomplete presentation of the principle of dissymmetry, and cannot be accepted without reservations.

On the Nature of Solutions.—A. Reyckler.—The author considers the dissolved substance when it is not and when it is an electrolyte, and then examines electrolysis itself.

Certain Double Salts of Quinine.—E. Grimaux.—An examination of quinine chlorhydrosulphate, bromhydrosulphate, and iodhydrosulphate.

Ampelochroïc Acids.—A. Gautier.—Each variety of *Vitis vinifera* produces one or more colouring-matters. All these colouring-matters, to which the author gives the name œnolic acids, possess feebly acid properties. If they are melted with caustic alkali they are split up into (1) phloroglucine, (2) aromatic acids generally, the protocatechuic or hydroprotocatechuic acids, (3) acids belonging to the fatty series or to the non-saturated series, C_nH_{2n}–2O₂ and C_nH_{2n}–2O₃. The author has distinguished in the coloured tannins or ampelochroïc acids three varieties, α , β , and γ . The colours of autumnal leaves cannot be ascribed to erythrophyll or to its modifications, but to phlobaphenes and catechines.

Revue Universelle des Mines et de la Metallurgie.

Vol. xix., No. 2, August, 1892.

Silicon and Aluminium in the Metallurgy of Steel.—Prof. Sergius Kern.—The author concludes that the best reductive addition for steel castings is silico-spiegel at 10 per cent of silicon and 12 per cent of manganese. After casting, the products ought to contain from 0.25 to 0.30 per cent of silicon. Mr. J. W. Spencer, manager of the Newburn Steel Works, made experiments to the same end, almost simultaneously with Prof. Kern, and arrived at results almost identical. Aluminium was found to be an excellent reducing agent, decomposing the oxides and giving a metal without blow-holes. But in castings of 165 to 250 kilos, it yields a crystalline structure which is very defective. In castings of small weight nearly 0.1 per cent of aluminium may be introduced. The presence of this metal increases the resistance to breakage.

Determination of Sulphur in Fuel by the Eschka Process.—Dr. Franz Hundeshagen.—From the *Chem. Zeitung*.

Series 3, Vol. xx., No. 2.

This issue contains no chemical matter.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 82.

Report made by M. de Luines on Behalf of the Committee of Chemical Arts, on the Bleaching-Process of M. Hermite.—The author obtains his bleaching agent by the electrolysis of a mixture of 1000 parts of water, sodium chloride 50 parts, and magnesium chloride 5 parts. Only the magnesium chloride and the water appear to be decomposed, forming at the positive pole a compound of great decolourising agency. There is no fear of the presence of free soda. The bleaching bath contains per litre from 0.5 grm. to 2 grms. per litre. An electrolyser of Hermite's system produces in twenty-four hours the equivalent of 100 kilos. dry chloride of lime at a cost of 5.22 francs, if hydraulic power is used; or 10.02 francs, if steam has to be employed.

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Medical, 8.30.

TUESDAY, 17th.—Institute of Civil Engineers, 8.

Pathological, 8.30.

Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.

Society of Arts, 8. "Mexico, Past and Present," by Edward J. Howell.

WEDNESDAY, 18th.—Society of Arts, 8. "The Mining Industries of South Africa," by Bennett H. Brough, Assoc. R.S.M.

Meteorological, 7. (Anniversary).

Microscopical 8. (Anniversary).

THURSDAY, 19th.—Royal, 4.30.

Royal Society Club, 6.30.

Royal Institution, 3. "Tennyson," by the Rev.

Canon Ainger, M.A., LL.D.

Society of Arts, 4.30. "The Currency Problem," by J. Barr Robertson.

Chemical, 8. "The Determination of the Thermal Expansion of Liquids," by Prof. T. E. Thorpe, F.R.S. "The Thermal Expansion and Specific Volumes of Certain Paraffins and Paraffin Derivatives," by Prof. Thorpe, F.R.S., and Lionel M. Jones, B.Sc. "The Hydrocarbons Formed by Decomposition of the Citene Dihydrochlorides," by W. A. Tilden, F.R.S., and Sidney Williamson. "Camphorosulphonic Derivatives," by F. S. Kipping and W. J. Pope. "Note on the Decaphanes Formed from Terpenes and Camphor," by Henry E. Armstrong.

FRIDAY, 20th.—Quekett Club, 8.

Royal Institution, 9. "Liquid Atmospheric Air," by Prof. Dewar, F.R.S.

Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.

SATURDAY, 21st.—Royal Institution, 3. "Expression and Design in Music," by Prof. C. Hubert H. Parry, M.A.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Pipes for Corrosive Liquid.—I should be much obliged if some correspondent would, through the medium of your paper, inform me what metal pipes could be used effectively for conveying strong (cold) solutions of corrosive sublimate?—W. G. KENT.

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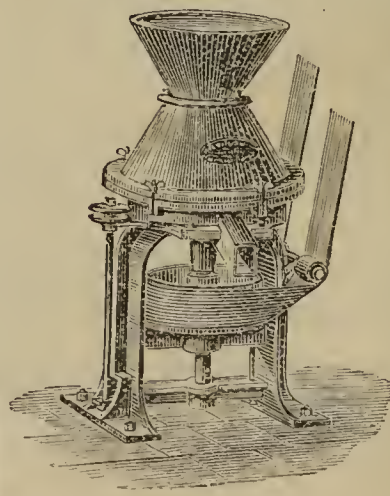
PARTNERS:—

N. H. MARTIN, C. E. STUART, B.Sc., H. SPARGO, A.Sc., F.I.C.

ST. PAUL'S SCHOOL, West Kensington.—

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1730.

ON THE ORIGIN OF COLOUR.

I. RELATION OF MOLECULAR AND ATOMIC VOLUME TO COLOUR.

By WILLIAM ACKROYD, F.I.C.,
Public Analyst for Halifax.

In the presence of an influx of new and old ideas regarding the origin of colour, I may be permitted to point out that some eighteen years ago I constructed a metachromatic scale, a generalisation resulting from the study of colour changing bodies, and I applied the scale to the study of colour in compounds, arriving at a law of colour for binary compounds (CHEM. NEWS, xxxiv., p. 76, and *Phil. Mag.*, Dec., 1876). In discussing the cause of these phenomena, I initiated the idea of "potentiality." The year after I published a method of making, and the measurements made, of the molecular aggregates concerned in these structural absorption phenomena (CHEM. NEWS, xxxvi., p. 159).

In 1884 Carnelley, using the metachromatic scale I had devised, and surveying the subject from the more comprehensive vantage ground of the periodic law of the elements, showed that there are indications that the colour of compounds is a periodic function of the atomic weight (*Phil. Mag.*, Aug., 1884). In the early part of 1892 I communicated to the Physical Society of London what I take to be the law of colour and constitution in a paper which is not yet published. The law may be thus briefly stated:—In a series of molecules with a constant radical R, and a weight-variable radical R', the colour varies in a definite order, increase of weight of the variable radical R' causing change of colour towards the black end of the colour scale (see below). In support examples were given in which R' was an electro-negative element; elements belonging to a natural series like Mg, Zn, Cd, and Mg, combined with a common simple or compound radical; water in crystalline salts; an organic radical like NH₂, or a metal in an isomorphous group.

The following argument has occurred to me, which may be taken as a further contribution to this interesting subject. A colour-changing body has its temperature gradually raised and its colour altered in the order of the metachromatic scale; during this change its specific gravity is decreasing, and we may assume that inversely its molecular volume is increasing. Hence we may correlate the change of colour from white through the scale to black with increase of molecular volume, thus—

White, blue, green, yellow, orange, red, brown, black.



Increase of molecular volume.

A similar difference of molecular volume in comparable compounds exhibiting conformity with the laws of colour referred to in the first paragraph, is apparent in the following examples which I have calculated:—

Pairs of Binary Compounds.

	Molecular volume.
HgO, red	19.5
Hg ₂ O, black.. .. .	43.4
Bi ₂ O ₃ , yellow	56.7
Bi ₂ O ₅ , brown	84.1
Sb ₂ O ₃ , white	49.9
Sb ₂ O ₅ , yellow	49.1

Crystallised Salts.

CuSO ₄ , white	44.0
CuSO ₄ .5H ₂ O, blue	113.0
PtCl ₂ , green.. .. .	45.3
PtCl ₄ .8H ₂ O, yellow	196.7

A Natural or Periodic Series of Compounds.

MgO, white	11.8
ZnO, white to yellow.. .. .	14.8
CdO, red to brown	15.6
HgO, red	19.5
ZnS, white	24.8
CdS, yellow	31.9
HgS, white to black	30.0

An Isomorphous Group of Oxides.

Al ₂ O ₃ , white.. .. .	25.0
Cr ₂ O ₃ , green.. .. .	30.3
Fe ₂ O ₃ , yellowish red	30.3

The coloured non-metallic elements also exhibit the same relations of colour to atomic volume, thus—

	Atomic volume.
Sulphur, yellow	31.2
Selenium, red	37.2
Chlorine, green, liquid	53.3
Bromine, red, liquid	53.9
Iodine, dark red, liquid	56.3

Carbon in its different forms conforms to the same law.

These examples from compounds and elements comparable among themselves therefore demonstrate a new law, viz., that increase of absorption of light in the order of the metachromatic scale is accompanied by increase of molecular and atomic volume.

At the present stage of the inquiry it is difficult to say what are real exceptions to this law on account of the uncertainty in some cases as to what may be the molecular weight of compounds which cannot be vapourised; thus cupric oxide with the formula CuO would be an exception when compared with cuprous oxide, Cu₂O. Is the formula of cupric oxide, however, CuO or α CuO? If we take it as Cu₂O₂, e.g., it conforms to the law.

Halifax, Jan. 12, 1893.

ON THE ANALYSIS OF FERROSILICON AND SILICEOUS SPIEGEL.

By T. W. HOGG.

THE recent publication in the CHEMICAL NEWS of Zeigler's paper on the examination of ferro-alloys suggests that there are in use many unnecessarily complicated analytical processes.

Amongst the alloys dealt with are ferrosilicon and siliceous spiegel; and as these are of most common occurrence, those who may have them to examine often and have not simple methods of their own may be glad to know that the silicon may be determined with great rapidity and accuracy. It has been stated on many occasions, and it is a general impression, that high percentage ferrosilicon and siliceous spiegel are very imperfectly attacked by nitrohydrochloric acid, and that these alloys cannot be decomposed in this way.

This misconception has arisen from two causes; in the first place, if the alloy is not in a fine state of division the particles are coated with a layer of silica which prevents all further action of the acid. In the second place, where the alloy has been sufficiently pounded, after the usual treatment with the acid, the mixture is always evaporated to dryness and gently heated in order to

render insoluble that silica which may have passed into solution. After then dissolving the residue in hydrochloric acid, filtering and washing, and igniting, the silica thus obtained is always contaminated largely with oxide of iron; this circumstance has naturally produced the impression that the alloy is only partially decomposed.

This, however, is not the case; if the ferrosilicon or siliceous spiegel be in a very fine state of division, vigorous boiling with nitrohydrochloric acid will perfectly decompose it in fifteen minutes. The silica which is formed is contaminated only with graphite. The physical condition of this silica, however, is so peculiar that if it be gently heated in contact with an iron salt in the dry state, it takes up ferric oxide and retains it with such tenacity that no ordinary amount of boiling with hydrochloric acid will purify it.

This peculiarity of course at once suggests that it is simply necessary to filter off the silica before evaporating, and evaporate the filtrate to dryness by itself in order to obtain the small quantity of dissolved silica.

In dealing with low percentage alloys, the quantity of silica which passes into solution is much greater than in the higher ones, and I have generally found the quantity to vary from 0.1—0.3 per cent in alloys containing from 10—15 per cent silicon. For works purposes, therefore, an addition of 0.2 per cent may be made to the quantity found by filtering off at once and the evaporation to dryness safely omitted. In this way the operator may have the silica ready to ignite in thirty minutes from the time of weighing out.

In conclusion, I would specially point out that the rapidity and perfectness of the decomposition in nitrohydrochloric acid depends entirely upon the fineness of the particles, and to secure this, after the usual treatment in the steel mortar and passing through the sieve, the small quantity necessary for the determination is ground as fine as possible in the agate mortar.

The method above described has been in use in the Newburn Steel Works' laboratory for nearly ten years, and it is rare that a silica is obtained which is not perfectly white after ignition over the blowpipe.

I need hardly allude to the fact that occasionally titanitic acid may be present, and in cases where great accuracy is required this may be separated in the usual way by treatment with sulphuric and hydrofluoric acids.

ON THE CATALYTIC ACTION OF ALUMINIUM CHLORIDE ON SILICIC ETHERS.*

By H. N. STOKES.

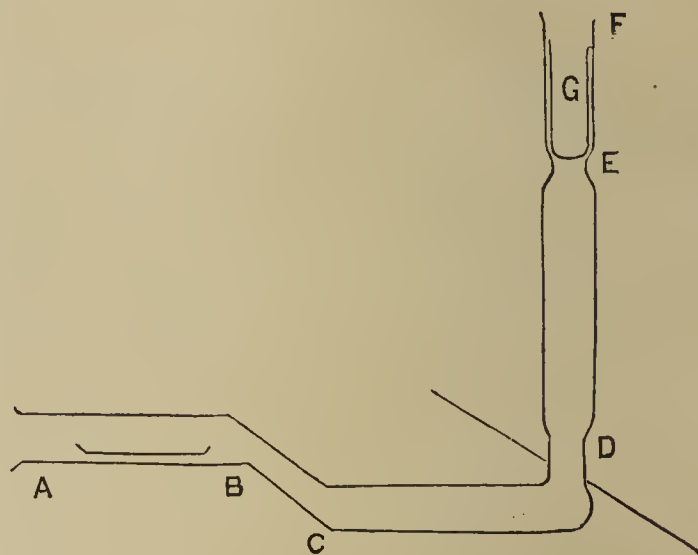
(Concluded from p. 17).

Experimental Details.

ONLY carefully fractioned silicates and freshly sublimed aluminium chloride were used. The apparatus and method of working were as follows:—

A thin-walled glass tube of about 2 c.m. diameter was drawn out into the shape shown in the figure. The constriction E served when necessary as a support for the small weighed test-tube G, in which the ethyl ether collected. Some aluminium chloride was placed in a boat, inserted into AB, and carefully sublimed over into CD in a current of dry hydrogen. In this way it was obtained in a finely divided state, rendering solution more rapid. The hydrogen was then replaced by air, BC drawn out and melted off at B, and the weight of the sublimed chloride determined to a centigram. CD was then placed in ice, the calculated weight of silicate or chlorsilicate introduced through F, the tube G inserted when necessary, and the apparatus attached to an inverted condenser which ended in a U-tube with two cocks, placed in a

freezing mixture, and serving to condense the ethyl chloride and any ethyl ether that might be carried over. By gently agitating the tube, the solution of the chloride was effected. On removing from the ice, the reaction usually began of itself, and often had to be moderated by cooling. After the evolution of ethyl chloride had slackened, CD was gently heated, the ethyl ether then distilling and collecting in G. After the collection of ether had ceased, G was gently warmed, whereby practically all ethyl chloride was driven over, the ether condensing and running back. After removing G, the

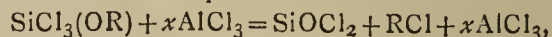


point B was broken off and the residue heated in a current of hydrogen until no further effect was observed, any aluminium chloride condensing in DE, or sometimes in part, being carried over into the condenser. The hydrogen was then displaced, DF melted off at D, when necessary, and all products determined by weighing. Some of the liquid in the U-tube was brought into a graduated tube over mercury, and any ethyl ether determined by absorption with a drop or two of strong sulphuric acid, the residue being ethyl chloride.

Ethyl Trichlorsilicate.

Taken $\text{SiCl}_3(\text{OR})$ 7.66 grms. (3 mol. wts.) and AlCl_3 1.91 grms. (1 mol. wt.).

On removing the ice from CD, the evolution of ethyl chloride began almost at once, and the liquid grew so warm that cooling had to be resorted to to prevent the contents from boiling over. Presently a large quantity of a colourless, apparently crystalline substance separated, nearly filling the liquid. Its nature was not determined, but it was found to fuse on gently heating. After the evolution of ethyl chloride had moderated, its formation was promoted by a gentle heat. The liquid then became gradually thick, and finally almost solid. B was then broken off, and the residue heated in a stream of hydrogen until no further sublimation of aluminium chloride was observed. Absolutely no ethyl ether was formed. The residue was somewhat discoloured, solid, transparent, and frothy. As explained above, the reaction occurs in accordance with the equation—



as is borne out by the following data, which in this as in all following experiments are given in percentage of the total material used.

	Found.	Calculated.
Residue	46.3	51.2
Sublimate (AlCl_3) ..	20.9	19.9
Distillate, RCl	22.5	28.8

The results are naturally only approximate, but quite as near as could be expected: The viscosity of the liquid towards the end interferes with the smoothness of the

* From the *American Chemical Journal*, vol. xiv., No. 6.

reaction, and it is impossible to condense the ethyl chloride completely, or to prevent some being carried off by the current of hydrogen. If the reactions given are correct, the residue is not really $\text{SiO} \cdot \text{Cl}_2$, but a mixture of oxychlorides in which there remains a small amount of ethyl, which will not go off at a temperature below that at which carbonisation and other secondary changes take place, and which are still greater in the cases below mentioned. Troost and Hautefeuille (*loc. cit.*) have shown that the result of heating oxychlorides is an approximation towards SiO_2 and SiCl_4 . This is doubtless the reason why in this case the weight of the residue is slightly too low, and that of the sublimed aluminium chloride a little too high. The former, on extracting with alcohol, left a little silica in gelatinous form, while the latter was found to contain a small amount of volatile silicon compounds. In fact, the residue, on heating in a test-tube to redness, gave off a considerable amount of volatile oxychlorides, but no aluminium chloride.

In experiment 2 the proportions taken were the same and the observations essentially similar.

	Found.	Calculated.
Residue	38.9	51.4
AlCl_3 (sublimed) ..	21.2	19.8
RCl	22.4	28.8

The residue consisted mostly of oxychlorides soluble in alcohol, and considerable silica insoluble in alcohol. A portion of the same residue gave—

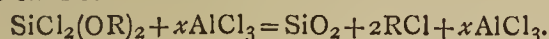
	Found.	Calc. for $\text{SiO} \cdot \text{Cl}_2$.
Si	27.08	24.35

The excess of silicon is due, as before, to a partial volatilisation of oxychlorides with a low percentage of silicon. This residue also contained a very small amount of aluminium, which was completely extracted by alcohol, and therefore present as chloride, not as silicate or oxide. No ethyl ether was formed.

In experiment 3, the residual aluminium was determined in the residue after heating to dull redness in hydrogen. The amount found, calculated as chloride, was only 3.5 per cent of the total chloride used. A small amount was to be expected, as it is practically impossible to expel it completely from the solid frothy residue. The conclusion that the chloride remains unchanged at the end of the reaction may therefore be accepted without hesitation.

Ethyl Dichlorsilicate.

This calls for the reaction—



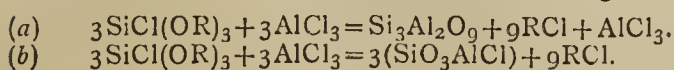
Two experiments were made, one with $\text{Si} : \text{Al} = 50 : 1$, the second with $\text{Si} : \text{Al} = 3 : 1$. In both cases the decomposition was readily brought about; in the first almost as easily as in the second, but only in the second could any aluminium chloride be recovered, and then not the whole amount used. A small amount of ethyl ether was also formed in each case. As there were reasons for suspecting the sample to contain monochlorsilicate (which would explain the discrepancy), and as no more was available, the quantitative data are omitted.

Ethyl Monochlorsilicate.

Four experiments were made, in which the following proportions were observed:—

$$\text{Si} : \text{Al} = \begin{cases} 3 : 3 & (1). \\ 3 : 2 & (2). \\ 3 : 1 & (3). \\ 150 : 1 & (4). \end{cases}$$

For case (1) the following equations hold, according as the chlorine of the aluminium chloride is completely given off as ethyl chloride, or as it remains in part as $\text{O} > \text{AlCl}$.



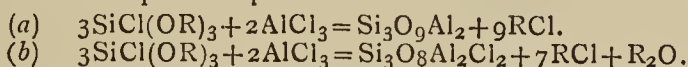
Taken, 6.21 grms. $\text{SiCl}(\text{OR})_3$ and 4.19 grms. AlCl_3 , or equal mol. wts.

The course of the reaction was essentially the same as with the trichlorsilicate, except that no solid was deposited. The liquid became gradually thicker, with evolution of ethyl chloride, and then quite suddenly stiff at about 75° . On heating in a current of hydrogen, a considerable volume of uncondensable hydrocarbon gas was given off, whereby some aluminium chloride was carried into the condenser and receiver. This was collected and determined. The amount of aluminium fixed in the residue was also determined. No ether collected, and none could be found by absorption over sulphuric acid.

	Found.	Calculated for (a).	Calculated for (b).
Residue	37.5	28.4	45.9
Al in residue ..	7.3	5.4	8.1
AlCl_3 (sublimed)	3.5	13.5	—
R_2O	—	—	—

The reaction occurs, therefore, in a form combining (a) and (b), the residue probably consisting in part of aluminium silicates, in part of chloraluminium silicates.

For case (2), where $\text{Si} : \text{Al} = 3 : 2$, there are also two ultimate equations possible—

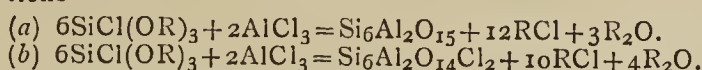


Taken, $\text{SiCl}(\text{OR})_3$, 12.93 grms.; AlCl_3 , 5.80 grms.; or exactly $3 : 2$ mol. wts. The reaction was essentially similar to that in the last experiment, and took place quite as readily as when more chloride was used. The same gradual thickening and sudden stiffening of the liquid were noticed. On finally heating to dull redness in hydrogen, gas was evolved, and a somewhat carbonaceous black vitreous residue was left, but no aluminium chloride sublimed. A small amount of ethyl ether was formed, which was determined by absorption.

	Found.	Calculated for (a).	Calculated for (b).
Residue	36.0	32.7	39.1
Al in residue ..	6.1	6.2	6.2
AlCl_3 (sublimed)	—	—	—
R_2O	2.5	—	8.6
RCl	33.5	67.3	52.3

Here, too, the reaction is intermediate between (a) and (b), some R_2O is formed, but all aluminium remains in the residue.

Case (3), where $\text{Si} : \text{Al} = 3 : 1$, also admits of two equations—



Taken, $\text{SiCl}(\text{OR})_3$, 14.72 grms.; AlCl_3 , 3.30 grms., or $3 : 1$ mol. wt. The same thickening and sudden stiffening at 75° were observed. The reaction began at the same low temperature, and was nearly as rapid as with more chloride. Ethyl ether collected in the tube G in abundance, and was identified by its boiling at 30° – 35° . The solid residue was nearly colourless, and only on high heating did discolouration ensue. No chloride sublimed. The ether was determined by weighing that collected, and absorbing the small amount found in the distillate as before.

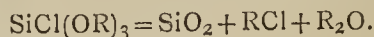
	Found.	Calculated for (a).	Calculated for (b).
Residue	43.1	31.7	38.4
AlCl_3 (sublimed)	—	—	—
R_2O	20.0	15.2	22.0

Although the residue was somewhat too large, the amount of ether showed that the reaction was mainly in the sense of (b).

Case (4). In this experiment 1 mol. wt. aluminium chloride was made to act on 150 mol. wts. monochlorsilicate, or almost a mere trace of the former (taken, 13.38

grms. silicate to 0.06 grm. chloride). The facts noted were the same as in the other experiments, including the sudden solidifying of the residue. The only difference was that the reaction took place rather more slowly, owing to the small amount of chloride present, and that the residue left at red heat was of purplish colour, showing very little carbonisation. The ease with which the decomposition took place indicated that a much smaller amount of aluminium chloride would have been sufficient. The ethyl ether showed the correct boiling-point.

The equation for a trace of aluminium chloride is practically—



The actual results were:—

	Found.	Calculated for Si : Al = 150 : 1.
Residue	30.8	30.3
R ₂ O	32.7	35.8
RCl	11.2	33.0

The amount of ether was 89 per cent of the theoretical.

Tetraethyl Silicate.

Four experiments may be mentioned, into which the following proportions entered:—

$$\text{Si : Al} = \begin{cases} 3 : 4 & (1). \\ 3 : 1 & (2). \\ 3 : 0.9 & (3). \\ 150 : 1 & (4). \end{cases}$$

The hypothetical equations for (1) and (2) are given under the general considerations on the decomposition of the tetraethyl silicate (*a*, *b*, and *c*).

For experiment (1) were taken 5.95 grms. Si(OR)₄, 5.09 grms. AlCl₃, or 3 : 4 mol. wts. It was not possible to cause the chloride to dissolve completely in this amount of ether, and the result was a mixture of varying composition, from which no definite result could be expected. The general course of the reaction was the same as in other cases. Some ethyl ether was formed, but a little aluminium chloride also sublimed, indicating an excess in one part of the mass and a deficiency in another.

In experiment (2) with Si : Al = 3 : 1 the mixture evolved ether and ethyl chloride, and finally became solid, and on further heating gave off gases, but no aluminium chloride. Only about one-half the theoretical amount of ether was obtained, the remainder appearing as hydrocarbon gas and empyreumatic substances.

In experiment (3) with Si : Al = 3 : 0.9 it was noticed that some unchanged silicate distilled at the end of the operation. It appears, therefore, that the least amount of aluminium chloride required to effect total decomposition is 1 mol. wt. to 3 mol. wts. of the silicate. This is strikingly seen in the next experiment (4), which at the same time shows the radical difference in their behaviour towards aluminium chloride of the silicates and chlor-silicates.

Taken, 16.37 grms. Si(OR)₄, 0.07 AlCl₃, or 150 : 1 mol. wts. Even on boiling strongly for an hour at about 165°, no marked reaction was noticed. The liquid remained clear and limpid, and not over 0.1 grm. ethyl ether collected. At the end of an hour the silicic ether was distilled off unchanged, leaving but a trace of solid residue. It was therefore clear that only a trace had been decomposed, corresponding to the trace of chloride used.

The decomposition of monochlorosilicates by a trace of aluminium chloride might perhaps be utilised to obtain other ethers than ethyl ether. It is known that the continuous process for obtaining ethyl ether from alcohol by means of sulphuric acid does not apply to the alcohols above propyl alcohol (Norton and Prescott, *Amer. Chem. Journal*, vi., 241). Isobutyl alcohol, for instance, does not give a trace of isobutyl ether. The silicates of the monatomic aliphatic alcohols, as far as has been investigated, are easily prepared, and of all the chlor-silicates

the monochlorosilicates are the most easily made. By adding to 1 mol. wt. silicon tetrachloride 3 mol. wts. of the alcohol, boiling the product or heating to 170° under pressure, and finally distilling with a trace of aluminium chloride, a product should be obtained consisting of a mixture of ether and chloride which could be easily separated. From ethyl monochlorosilicate 89 per cent of the theoretical yield of ethyl ether was thus obtained.

On the Isolation of the Intermediate Products.

Aluminium chloride is insoluble in carbon bisulphide if, however, a mixture of about 1 vol. tetraethyl silicate and 4 vols. carbon bisulphide be boiled with some aluminium chloride, the latter liquefies and partly dissolves, while there is an evolution of permanent gas, presumably ethyl chloride. On decanting the warm liquid a considerable amount of oil separates. This oil is not volatile, and on heating gives a solid residue resembling that obtained by the direct action of the chloride on the silicic ether. The carbon bisulphide solution, if concentrated out of contact with moisture, deposits on cooling a mass of well formed rectangular crystals, or on evaporation *in vacuo* over paraffin shavings leaves a perfectly dry crystalline mass. A portion of such a bisulphide solution was decomposed by ammonia, and the ratio of Si : Al : Cl determined. It was found to be 1 : 2.1 : 3.9, or very nearly 1 : 2 : 4, a result which may, of course, have been accidental. The oil which separates is soluble in a fresh portion of hot carbon bisulphide, but it appears readily to change, for a greater amount is required than that from which it separated, and by boiling out with small quantities of bisulphide, a residue is left which is finally almost solid. These facts seem to indicate the possibility of isolating some of the intermediate products, but this has not yet been attempted.

In conclusion, I wish to express my thanks to the Director of the Geological Survey, and to Prof. F. W. Clarke, for the means and opportunity of carrying out these experiments.

THE VOLUMETRIC ESTIMATION OF ZINC.

By BERTRAND C. HINMAN, Ph B., A.M.

THE Colorado Scientific Society outlined a plan, some time ago, of endeavouring to establish a uniformity in the technical methods of analysis in the West. For its first effort, a committee of several chemists was appointed to investigate the methods for the determination of zinc in ores, and their report was presented in June, 1892.

The ores submitted were from widely separated localities in Colorado; they were mixtures of galenite, pyrite, and sphalerite, accompanied by greater or less percentages of manganese in the form of rhodochrosite, associated with a quartzose gangue.

To obtain a standard of comparison, the samples of ore submitted by the committee were analysed by Mr. L. G. Eakins, of the U.S. Geological Survey. The method followed by him was the conventional one—in short, as follows:—

The ore was extracted with aqua regia, and the solution precipitated with sulphuretted hydrogen. In the filtrate from this precipitation, the iron was separated by precipitating twice as basic acetate, and once with ammonia. In these filtrates, combined and acidulated with acetic acid, the zinc was precipitated as sulphide, dissolved, precipitated as carbonate, and weighed as oxide.

Several chemists of metallurgical works in Colorado made analyses of the samples, and their methods and results are given in the report. They were, however, essentially like, or modifications of, the method of Messrs. Von Schulz and Low, which received the approval of the committee. (See *ante*, p. 6).

The ores upon which these experiments were made were all from one section of country, and, in general, were ores adapted to lead smelting. It seemed advisable, therefore, to try the method upon ores from other places containing associated minerals different from the above. The Franklinite and calamine ores are among the most important sources of zinc, and are very frequently dealt with in the metallurgy of that metal. Upon such ores most of the experiments were made.

The solutions were prepared as directed, with the exception that, for standardising, metallic zinc was used instead of the oxide. The standardising of the ferrocyanide solution presented no difficulty. If the solution is hot, the end-reaction shows promptly, but the amount of hydrochloric acid present must be regulated with some care, as an excess over that used at the time of standardising will delay the end-reaction in titration to a sensible degree. The practice adopted in making these experiments was to add a drop or two of methyl orange (though other indicators will answer equally well), bring the solution to the neutral point, and then add a known excess of hydrochloric acid. The colour produced by the indicator in no wise interferes with the end-reaction during titration. By observing this simple precaution, the solutions may always be of the same degree of acidity, insuring perfect uniformity in the appearance of the end-reaction.

At times, in dissolving the ore, all the potassium chlorate will not be decomposed, so that, when the solution is made acid with hydrochloric acid, just prior to titration, euchlorine will be set free. When using an indicator to determine the neutral point, its presence is manifested by its bleaching action upon the colour. It is well, then, to add a few drops of a solution of an alkaline sulphite.

To test the process, a calamine ore containing 66.80 per cent of zinc was carefully treated by the above-described method. There was obtained 65.14 per cent of zinc. The ore contained but little manganese, and the precipitate produced by the addition of the excess of ammonia consisted almost entirely of ferric hydrate. The residue and the precipitate was treated again with the chlorate mixture, the solution obtained evaporated to dryness, an excess of ammonia again added, and in the filtrate from this precipitation was found 1.62 per cent of zinc, making a total of 66.76 per cent. The experiment was repeated twice more in the same manner as at first. The three results were as follows:—

	First Extraction.	Second Extraction.	Total.
Per cent of zinc ..	65.14	1.62	66.76
" " ..	65.37	1.41	66.78
" " ..	65.35	1.41	66.76

The precipitated ferric hydrate held each time about 1½ per cent of zinc. This is a well-known phenomenon, but no mention of it seems to have been made by Messrs. Von Schulz and Low in their description. This is undoubtedly because the ores worked by them contained so little iron that no appreciable difference was made by its presence.

In a fourth experiment on this ore an attempt was made to avoid the re-precipitation of the ferric hydrate by evaporating the solution of the ore in the acid to dryness, and taking up with water instead of ammonia. Ferric nitrate seems to lose its nitric acid more readily than zinc nitrate, and by proceeding in this manner a filtered solution may be obtained containing only a small amount of iron. There was, however, enough present, so that it was necessary to remove it with an excess of ammonia. There was found as a result 66.45 per cent of zinc.

In order to determine the effect which the presence of manganese might have, a gm. of this ore was mixed with 0.200 gm. of pyrolusite, and treated precisely as at first. There was found 66.76 per cent of zinc, the manganese not changing the result. Thinking, perhaps, that

the manganese dioxide would not be sufficiently decomposed in the strongly oxidising solution used in decomposing the ore, another experiment was made upon the same ore with the same amount of pyrolusite present, but the mixture was first treated with hydrochloric acid to carry the dioxide of manganese into solution; nitric acid was added to expel the hydrochloric acid, and then the mixture was treated with the chlorate solution, and the analysis finished in the same manner as the previous ones. There was found 66.808 per cent of zinc.

It may be safely concluded, then, that the presence of manganese does not interfere, and that it can be completely separated from zinc by oxidation to manganese dioxide in nitric acid solution.

A Franklinite ore containing 20.86 per cent of zinc and considerable manganese was next tried. The first treatment of this ore gave as its result only 15.60 per cent. The residue re-treated with acid as before yielded 1.01 per cent, and the residue from this again treated gave up 0.50 per cent, making a total of 17.11 per cent of zinc, or nearly 4 per cent low. The experiment was repeated upon another portion of the same sample. There was found only about 15 per cent of zinc. The residue was re-treated as before, and a little over 1 per cent was found. The residue from this treatment was dissolved in hydrochloric acid, the iron separated as basic acetate, the filtrate made acid with acetic acid, sulphuretted hydrogen gas passed into it, and an abundant precipitate of zinc sulphide was obtained.

Evidently the solvent action of the nitric acid containing the potassium chlorate was not sufficient to completely decompose the ore, so in the next experiment the following treatment was adopted:—

The ore was first digested with aqua regia; nitric acid was then added, and the mixture evaporated until all the hydrochloric acid had been expelled, the whole evaporated nearly to dryness, the regular amount of the nitric acid solution of the potassium chlorate was added, and the analysis finished as usual. As a result of this procedure, there was obtained 20.81 per cent of zinc.

A Franklinite, containing 23.53 per cent of zinc, analysed in duplicate in this manner, gave results respectively 23.54 per cent and 23.34 per cent of zinc. Still another sample of the same kind of ore having 31.42 per cent was found by the same treatment to contain 31.613 per cent.

Some of the ores tried, although very finely pulverised in an agate mortar, were yet not entirely soluble in aqua regia, and it was necessary to fuse the residue in order to effect complete solution.

Copper was found to be easily separated in the manner described by the originators of the method, and the lead introduced, and that which might otherwise be present, was found to have no injurious effect. In fact, at the end of a titration with the brown tint just faintly showing with the uranium acetate, a large excess of lead acetate was added without changing at all the end reaction.

The method of von Schulz and Low, as given by them, will answer for ores easily decomposed and containing little or no iron, but to adopt the method to all ores of zinc or compounds containing it, cadmium alone excepted (which, if present, must be removed with sulphuretted hydrogen) certain modifications are necessary. Guided by the preceding experiments, the following practice would seem most advisable.

Pure metallic zinc is more easily obtainable for standardisation than the pure oxide. In standardising and in actual analysis, that the right degree of acidity be uniformly maintained, the use of a colour-indicator in the solution is advised. It seems to be easier and simpler to work to the neutral point this way than to do it by means of test-papers, and the slight tint of colour necessary to show the change to the eye does not impair the end reaction with the ferrocyanide.

The ore, if at all refractory, should be very finely pulverised. A few moments spent in grinding will be more

than compensated in the ease with which solution may be obtained.

Treat the finely divided ore with *aqua regia* until there is obtained complete decomposition, or until no further action is perceptible. If the ore has not been thoroughly decomposed, evaporate to dryness, dehydrate the silicic acid, take up with dilute hydrochloric acid, filter off the insoluble matter, and fuse it with carbonate and nitrate of soda in a platinum crucible. Dissolve the fusion in hydrochloric acid, and add the solution to the major portion. The dehydration of the silicic acid will consume some time, but if the ore is highly siliceous, the gain of time in filtering the sandy precipitate of silica as contrasted with filtering the gelatinous silicic acid will be more than repaid. All the zinc in the ore will now be in solution as chloride. Add nitric acid and boil until all the hydrochloric acid has been expelled; evaporate nearly to dryness, add the usual quantity of nitric acid saturated with potassium chlorate, and evaporate to dryness. Add the ammonium chloride and ammonia, dilute with water, heat to boiling, and filter, washing with a weak solution of ammonium chloride made alkaline with ammonia. Transfer the precipitate from the paper, by means of a spatula and wash bottle, to the vessel in which the ore was originally decomposed, evaporate off the water, and treat again with the chlorate mixture in the same manner as before, adding the solution obtained by treatment with ammonia to the original one. Acidify to the right degree with hydrochloric acid, heat nearly to boiling, and titrate with the standard ferrocyanide as described.

The details of the method as here worked out are more numerous than those given in the original article of von Schultz and Low, but it is apparent that to secure accuracy of results under varied conditions, they are necessary. It is still very much shorter than the conventional one, and carefully worked ought to give results nearly, if not quite, as accurate, and certainly the difficulties in manipulation are not so great.

In conclusion I desire to thank Professor Elwyn Waller for his valuable suggestions in the preparation of this paper.—*School of Mines Quarterly*, xiv., No. 1.

SOME REMARKS ON THE EXAMINATION OF THE RARE GADOLINITE EARTHS, AND IN PARTICULAR ON DETERMINING THE EQUIVALENTS OF THESE EARTHS BY CONVERTING THE OXIDE INTO THE SULPHATE.

By GERHARD KRÜSS.

LAST year I made known contributions to the chemistry of erbium and didymium (*Liebig's Annalen*, 265, 1), in which there are described some new methods for working up the earths of gadolinite. This investigation has been continued, especially as regards the earths of erbia, and before reporting in the following pages of this journal (*Zeit. der Anorganischen Chemie*) on the nature of erbium, holmium, and terbium, I wish to communicate some general observations on the elaboration of the rare earths in question; as also new methods for their separation.

L. F. Nilson and the author (*Berichte Deutsch. Chem. Gesell.*, xx., 2134) examined, six years ago, the region of the rare earths yielding absorption spectra by means of the qualitative spectrum analysis of a large number of earthy materials. Experiments in the same direction were made soon after by P. Kiewewetter and G. Krüss. From these observations it appeared that, e.g., erbia and holmia are of a more complex character than it has been hitherto supposed.

Subsequently I pursued the examination of those earths, no longer exclusively by qualitative spectrum analysis, as hereby, at most, the behaviour of the earths could be ascertained in a certain relation

to light. I did not carry out a plan which I had drawn out some years ago to institute a quantitative spectroscopic analysis of the solutions of the earthy salts. In this way merely some insight into the composition of mixed solutions of the earths could be expected without yielding better means for separating the mixtures. I wish to point out that the proof whether a rare earth is really homogeneous or not cannot in all cases be obtained spectroscopically as easily as it is sometimes assumed.

In all investigations—qualitative or quantitative—of the absorption spectra of the earthy salts, the colourless constituents, of course, escape direct observation. On the other hand, it must be considered that in examining the emission spectrum of a mixed earthy chloride, the lines of all the single constituents are not always visible. Mixtures containing even several per cents of ytterbia yielded in many cases no ytterbia lines in the very same experimental conditions in which pure compounds of ytterbium gave a visible spark spectrum. This fact has been previously observed by Nilson, Thalén, and others.*

Nevertheless, both absorption and emission spectroscopy are certainly frequently important auxiliaries in examining rare earths; but these methods if used alone do not suffice for the certain recognition—even qualitatively—of all the constituents of an earthy mixture. Here, as well as in deciding on the homogeneity of a fixed earth, we can never dispense with the methods for determining the equivalent. They are in the study of the earths a means equal in importance to spectrum analysis; without them there is at present no control of the value of one or other of the qualitative methods for the separation of the earths. The experiments which the author described a year ago, in *Liebig's Annalen*, 265, 1, have been conducted from this point of view.

Recently there has appeared (*Ber. Deutsch. Chem. Ges.*, xxv., 390, 569) an extensive investigation of P. Schottländer in which the spectroscopic method has been exclusively employed. The author's procedure of checking the results of qualitative spectral analysis by spectrophotometric measurements is, without doubt, of great theoretical interest, but the chemistry of the didymium oxides investigated does not seem especially advanced hereby to that extent that we have now with one or the other oxide of the didymium earths presented to us in a really pure state. Theoretically, Schottländer, by his spectrophotometric measurements, arrives at the conclusion that the rare earths producing absorption spectra have not in general so complicated a composition as Krüss and Nilson have previously inferred from the qualitative examination of those spectra. This seems to hold good, though in a quite different sense, from what P. Schottländer and the author also conjectured years ago. In the meantime, an examination of the nature of erbia and the kindred oxides has been carried on for several years, and I shall therefore return to that point by the present opportunity. I must here remark that after reading Schottländer's last treatise I regretted that he undertook the laborious quantitative spectroscopic examination of twenty-four didymia spectra, when he could ascertain from several preliminary experiments made with solutions of chrome-alum that his eye was but scantily prepared for the investigation. For this purpose a systematically conducted preliminary training of the eye is necessary, extending over several weeks.

On the Determination of the Equivalents of the Earths by Converting the Oxide into Sulphate.

If we desire to decompose a mixture of earths by any mixture whatever, and to form an opinion on the value of

* Thus, L. F. Nilson, in his treatise on scandium (*Ber. Deutsch. Chem. Gesell.*, xiii., 1442), describes an earth containing 1.3 per cent ytterbia and 98.7 scandia, and says:—"As Thalén, notwithstanding this considerable proportion of ytterbia, could find no foreign matter on its spectroscopic examination, the balance seems to be a far more sensitive instrument than the best spectroscope for testing the purity of two substances of so different atomic weights as Se = 44 and Yb = 173."

the method and the manner in which it acts, the method must sometimes be applied repeatedly, prolonged operations have to be carried out until distinct differences perceptible spectroscopically are obtained, and a certain decision may be reached.

In many cases differences in the composition of mixed earths may be found more rapidly, and in any case more certainly, by a determination of the equivalents of the earths.

This method has been already employed by several investigators. I need merely remind the reader of the isolation of scandia by L. F. Nilson. Generally speaking, however, this method is not preferred. The reason is probably that such careful gravimetric operations as the determinations of the combining weights of the rare earths are troublesome and tedious, especially when it is necessary for the object in view to effect hundreds of such analyses. Objections of another kind have also been advanced: calling in question the trustworthiness of the methods employed for determination and in part with right. The rare earths are generally not remarkably powerful bases; indeed, for the most part, they are feeble bases, so that the formation of basic salts may easily take place unless the earths are combined with decidedly strong acids. Hence the equivalents of the rare earths which have been deduced from the analysis of the chlorides, nitrates, and oxalates,* are possibly in many cases too high. The earthy sulphates should naturally yield the most trustworthy results, and their analysis has therefore been most frequently used for determining the equivalents of the earths.

On account of the tendency of barium sulphate to occlude other substances, it cannot be recommended to refer the equivalent of an earth to BaSO_4 , as it has often been done.

This reference requires a greater number of operations, and consequently includes more sources of error than if a weighed sulphate is converted into an oxide of ignition, or an oxide is transformed into a neutral sulphate.

As in the four last years very many determinations of the equivalents of the earths have been carried out in my laboratory, it seems to me that the conversion of oxide into sulphate is generally preferable to the inverse process. This method yields more certain results, and at the same time, in the execution of many determinations, it admits of the simultaneous performance of a great number of experiments.

According to the literature to which I have access, this method was first applied by J. Bahr and R. Bunsen (*Zeit. Annalen*, 137, 21, 1866) in the examination of yttria. In like manner the conversion of oxide into sulphate was utilised by J. T. Cleve (*Bulletin Soc. Chimique* [2], 21, 196, and 246, 1874) in determining the equivalents of lanthana and didymia, as also in the determination of ytterbia and scandia by L. F. Nilson (*Ofvers af Forh.*, 1880, No. 6, and *Ber. Deutsch. Chem. Gesel.*, xii., 550, and xiii., 1439). Although the names of these authors are a guarantee that this method is practicable, we find in those communications as to the manner of working by this method not more thorough-going instructions than the following:—That the oxide, chloride, or nitrate for conversion into sulphate is to be heated off with an excess of sulphuric acid at a temperature sufficient to expel free sulphuric acid, but not to form basic sulphate. Under certain circumstances this may be difficult, and in fact the earthy sulphates may be re-converted into earths by heating. I may further show that as G. H. Bailey (*Chem. Soc. Trans.*, 1887, 676–683) has pointed out some time ago, it is not possible to bring a didymium sulphate which contains excessive sulphuric acid to a constant weight by heating to 360° ; on every further gradual rise of temperature a loss of weight occurs again, and at no degree of temperature can didymium sulphate, contaminated with

an excess of acid, be brought to a constant weight. If Bailey's observations are correct, and if we consider that didymia is more strongly basic than scandia, ytterbia, or yttria, the conversion of these earths into sulphates, as undertaken by Bahr, Bunsen, and Nilson, can scarcely have been accurately practicable.

The author's own research was concerned with more feebly basic earths, the erbia-earths, the sulphates of which must certainly be still less stable than didymium sulphate. On this account I submitted the method of the determination of equivalents, the conversion of earths into sulphates, to the closest possible examination, especially as regards the stability of the earthy sulphates at the temperature at which the excessive sulphuric acid is expelled.

The earth, the equivalent of which is to be ascertained, was in the examples given below, and in all determinations of equivalents communicated by the author and his coadjutors in this and the following numbers of this journal, always again purified before its conversion into sulphate in the manner following:—Any traces of copper or platinum which might have been introduced in the course of the work were removed by passing sulphuretted hydrogen into the slightly acid solution of the earth; the earthy hydroxides were removed from the filtrate by means of ammonia, and washed for a long time to remove lime and magnesia. After dissolving in a little nitric acid and prolonged heating, the earths were precipitated as oxalates, filtered in a crystalline condition, and converted into earths by ignition in a porcelain crucible on the blast until the weight became perfectly constant.

If water or dilute hydrochloric acid is added to the oxides, a slight loss is easily occasioned by the formation of dust, wherefore the crucible containing the earth, protected by a dust-funnel, is placed first on a heated water-bath until the oxides have been slacked by the gradual access of watery vapour; solution is then effected by the addition of dilute hydrochloric acid and continued heating. After complete solution has been obtained, dilute sulphuric acid was added in moderate excess and concentrated as far as possible upon the water-bath. The sulphate then separates out in crystals. The elimination of the excessive sulphuric acid was effected first on an iron plate 2 decimetres square and 5 m.m. in thickness. To prevent spirting it was heated at first with a small flame, the point of which was at the distance of 4 c.m. from the plate. In this manner the concentration and evaporation of the excessive acid could be almost left to itself. The temperature was gradually raised, and after three hours the plate could be heated as strongly as it was possible by means of a powerful Bunsen flame placed immediately underneath.

After the visible evaporation in this manner has ceased, after about two hours it was heated with a triple burner, whereby the plate, if it rested upon an iron stand, never became red-hot under the crucibles.* The sulphate not yet perfectly driven off must not be left uncovered over night, as it would take up moisture and effloresce to loose masses like cauliflowers, and on further treatment it could scarcely be brought to a constant weight on account of its excessively large surface.

(To be continued).

Determination of Kreatinine in Urine.—Gautrelot and Vieillard (*Soc. de Medecine Pratique*).—The authors make three separate determinations of nitrogen, one in the original urine, a second in the same after precipitation with basic lead acetate, and a third after precipitation with basic lead acetate and zinc chloride.

* The "fuming off" of the excessive sulphuric acid up to this point can, of course, be effected much more rapidly. This requires, however, continuous careful observation of the contents of the crucible, whilst if the above conditions are observed, the excessive sulphuric acid of many analyses can be simultaneously driven off without particular trouble.

* The use of the oxalates for determining the equivalents of the earths will be considered in a subsequent memoir.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 15th, 1892.

Dr. W. J. RUSSELL, F.R.S., Vice President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. John Pedrozo d'Albuquerque, Barbadoes, W.I.; William James Cowan, 77, Trinity Road, Wood Green, London; George Davey, Las Trojes Angangués, Michoacan, Mexico; Daniel O. Sydney Davis, Rhydfallen, Stonebridge Park, Willesden, N.W.; Samuel Felix Dufton, D.Sc., Spring Wood House, New Cross Street, Bradford; John Henry Evans, 71, Lambton Road, Cottenham Park, Wimbledon; Charles Thomas Tyrer, Stirling Chemical Works, Stratford, E.; James Robert Thackrah, M.A., Technical Schools, Plymouth; John Cundell Wood, 3, Bedford Terrace, Sunderland.

The following were duly elected Fellows of the Society:—David Avery; Samuel Robert Adcock; William Smellie Anderson; Horace Vincent Butterfield; Arthur John Bensusan; Arthur James Cooper; Frederick Walter Carlton; Earnest Victor Clark; Andrew Campbell; Andrew William Craig; Lionel Cooper; Joseph R. Dennison; Thomas Duxbury; Martin Onslow Forster; William French; Walter Goodall; William Thomas Gronow; Thomas Gray; James G. Hardy; Walter S. Haines; Samuel C. Hooker, Ph.D.; Edgar Edward C. Horwill; John Horsfall, Walter Holinshed Ince, Ph.D.; John F. V. Isaac; Samuel Jackson; John Jackson; William George Johnston; G. Krause, Ph.D.; Kunwar Kishor Kacker; Thomas Torrens Knowles; Charles Thornton Lamb; Francis Colin Moorwood; John Bate Nicholls; James Wyllie Rodger; Hugh Ramage; Norman Scott Rudolf; James Robson; Augustus Schloesser, Ph.D.; Ernst Speidel, B.S.; George Arthur Shaw; Reginald des Forges Shepherd; William James Sell; Satvaprasad Sarbadhicary; Charles Spackman; Albert Henry Turton; N. T. M. Wilsmore; William Williams; Jno. Lowe Whiteside; Jno. Williams; Frederick Henry Wigham, Frederick William Westaway.

Of the following papers, those marked * were read:—

*82. "The Identity of Caffeine and Theine and the Interactions of Caffeine and Auric Chloride." By WYNDHAM R. DUNSTAN and W. F. J. SHEPHEARD.

Mays (*Journ. Physiol.*, vii., 458; *Therapeutic Gazette*, 1866, 587) and more recently Lauder Brunton and Cash (*Roy. Soc. Proc.*, xlii., 238; *Journ. Physiol.*, ix., 112) having concluded that "theine" from tea differs in its physiological action in certain respects from "caffeine" from coffee, the authors have deemed it desirable to compare the products from the two sources: they conclude that their identity is beyond question. The observed differences in physiological action must be ascribed either to impurities in the materials used, or to differences in the animals to which they were administered; the circumstance that "theine" has been found to be more active and to be capable of producing effects not produced by "caffeine" tends to support the view that the "theine" was impure, especially as it is known that tea contains other alkaloids.

It is found that when an aqueous solution of caffeine aurichloride is heated, a yellow flocculent precipitate of aurochlorocaffeine is gradually formed, the—



being resolved into 2HCl and $\text{C}_8\text{H}_9(\text{AuCl}_2)\text{N}_4\text{O}_2$; this substance is insoluble in alcohol, chloroform, and ether, but dissolves in chlorhydric acid, being re-converted into the aurichloride; it is contended that the production of this compound is better shown by Medicus's formula of

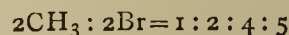
caffeine than by that proposed by Emil Fischer. A compound of caffeine and potassium aurichloride is described, crystallising in dark red needles; it readily dissolves in alcohol and water, but apparently dissociates.

DISCUSSION.

Professor TILDEN, referring to his work on periodides of alkaloids published over twenty-five years ago (*C. S. Journ.*, xviii., 99; xix., 145), said that he had not been able to notice any difference between the periodides prepared from caffeine and theine.

*83. "Studies on Isomeric Change. (II.) Orthoxylene-sulphonic Acids." By GERALD T. MOODY, D.Sc.

The results described in this and the following note have been obtained in the course of an investigation on isomeric change now being carried on at the Central Institution (*cf. Proc. Chem. Soc.*, 1888, 77); the object in view was to determine whether 1:2:3-orthoxylene-sulphonic acid is converted on heating into 1:2:4-orthoxylenesulphonic acid. In order to prepare the 1:2:3-acid, orthoxylene was first treated with two molecular proportions of bromine, whereby it was converted into a mixture of the liquid and solid dibrom-orthoxylenes; the latter (m.p. 88°) — which has been shown by Jacobsen to have the constitution—



—was sulphonated by very cautiously heating it in a water-bath with about ten times its weight of 15 per cent anhydrosulphuric acid until the mixture became liquid, then keeping it at 75°, with constant shaking, until complete dissolution of the oil was effected; the liquid solidified on cooling. The resulting sulphonic acid was converted first into barium salt and eventually into sodium salt. Sodium dibromorthoxylenesulphonate, $\text{C}_6\text{HBr}_2(\text{CH}_3)_2\text{SO}_3\text{Na} + 1\frac{1}{2}\text{H}_2\text{O}$, crystallises in small scales, and is easily reduced on boiling it with zinc dust and sodium hydroxide, forming 1:2:3-sodium orthoxylenesulphonate. The latter crystallises in beautiful long flat monohydrated plates; unlike the sodium salt of the 1:2:4-acid, it does not effloresce in air. 1:2:3-orthoxylenesulphonic chloride crystallises from light petroleum in prisms melting at 47°, the sulphaamide crystallising from water in groups of needles melting at 167°.

The 1:2:3-sulphonic chloride was converted into the acid by heating 5 grms. of it with 20 c.c. of water in a sealed tube immersed in the vapour from boiling xylene, the tube being, from time to time, removed from the bath and shaken; the resulting solution was cautiously evaporated on a steam-bath. The crystalline acid thus formed remained dry on being exposed to the air for several days; a small portion was converted into sulphonamide, which melted sharply at 167°, showing it to be the unchanged 1:2:3-acid; the rest was placed in a tube standing in an oil-bath heated at 115–120°, and a current of dry air drawn over it during two hours, at the end of which time the acid has become dark grey in colour. The sulphonamide prepared from the thus-heated acid melted sharply at 144°, showing that the 1:2:3-acid had been completely converted into the isomeric 1:2:4-acid. On repeating the experiment, the same result was obtained; and it is worthy of remark that in both cases only a very slight indication of the formation of sulphuric acid was obtained.

*84. "Studies on Isomeric Change. (III.) Phenetoil-sulphonic Acids, $\text{C}_6\text{H}_4(\text{OEt})\text{SO}_3\text{H}$." By GERALD T. MOODY, D.Sc.

In a note published early in the year (*Proc. Chem. Soc.*, 1892, 90) the author stated that only one sulphonic acid is formed by the interaction of sulphuric acid and phenetoil under ordinary conditions; Lagai not long afterwards controverted this statement (*Ber.*, 1892, 1839) and asserted that he had isolated a second acid from the product of sulphonation; describing its chloride as a syrupy liquid, and its amide as crystallising from water in feathery

needles melting at 142°. Lagai, however, quoted no analyses, or other evidence to show that his compound melting at 142° was really a derivative of phenetol.

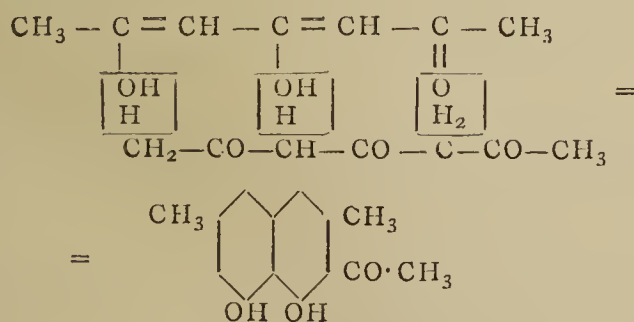
In order to obtain the orthophenetolsulphonic acid, parabromophenol was ethylated. The bromophenetol thus formed boiled constantly at 228—230°, and readily sulphated when shaken with an equal bulk of ordinary oil of vitriol. The resulting bromophenetolsulphonic acid crystallised from the acid solution in characteristic prisms. It was readily reduced by digestion with zinc dust and sodium hydroxide solution. The sodium salt of the resulting ortho-acid, $C_6H_4(OEt)SO_3Na + H_2O$, crystallised in slender needles; it afforded a sulphonic chloride which crystallised from light petroleum in thin plates melting at 62°, from which a sulphonamide was obtained, crystallising in very long flexible needles, melting at 156°. These melting points place beyond doubt the fact that Lagai's compound melting at 142° is not phenetolortho-sulphonamide. On the other hand, the sulphonic acid giving a chloride and amide melting at 62° and 156°, respectively, is shown to be a phenetol derivative by its behaviour on heating. The pure acid was formed by digesting the sulphonic chloride melting at 62° with dilute alcohol for twelve hours, and then evaporating the solution; it was obtained as a crystalline mass, permanent in air. A small quantity of this product was converted into sulphonamide, which was found to melt at 156°; the remainder was placed in a tube contained in an oil bath and heated for three hours at 100°, a current of dry air being passed through the tube; during the process, the acid darkened somewhat in colour, and was eventually found to contain a minute quantity of sulphuric acid. The acid thus heated gave a sulphonamide which melted sharply at 150°, showing that a complete change to the para-acid had taken place.

*85. "Formation and Nitration of Phenyl diazoimide." By WILLIAM A. TILDEN and J. H. MILLAR.

Phenyl diazoimide, $N_3 \cdot C_6H_5$, is readily prepared by the interaction of nitrosyl chloride and phenylhydrazine dissolved in excess of glacial acetic acid, together with only a small quantity of resinous by-products. When gently heated with ordinary strong nitric acid, the imide yields about two-thirds of its weight of the paranitro-derivative (m. p. 74°), together with smaller quantities of two crystalline by-products not yet fully examined. Nitrophenyl diazoimide forms a convenient source from which to obtain Curtius's diazoimide, about 40 per cent of the calculated quantity of the compound being obtained, as shown by Noelting, Grandmougin, and Michel (*Ber.*, xxv., 3328), on boiling it with alcoholic potash.

*86. "The Production of Naphthalene Derivatives from Dehydracetic Acid." By J. N. COLLIE.

The author has further examined the yellow substance referred to in his previous notice (*Proc. Chem. Soc.*, 1892, 188), and arrives at the conclusion that the condensation of diacetylacetone probably occurs in the following manner:—



At first he was inclined to the belief that the substance was a quinone, but, as all attempts to reduce it failed, and as it did not, in other respects, behave as a quinone, he has abandoned the idea; moreover, it is impossible to explain the formation of a quinone from diacetylacetone

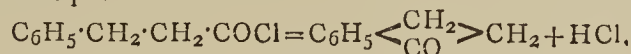
by any simple interaction such as the mere elimination of the elements of water involves.

The substance yields a diacetyl derivative when heated with acetic anhydride, and affords bromine substitution derivatives when treated with bromine. A trimethylnaphthalene is produced on distilling the diacetate with zinc dust.

Finally, it is pointed out that the 2-aceto-1-naphthol described by Wilt (*Ber.*, xxi., 321) and the 3-aceto-1-naphthol prepared by Erdmann (*Ibid.*, p. 635) closely resemble the compound from diacetylacetone.

87. "A New Synthesis of Hydrindone." By F. STANLEY KIPPING, Ph.D., D.Sc.

In a previous note (*Proc. Chem. Soc.*, 112, 107) it has been stated that a hydrocarbon of the composition C_9H_8 and other compounds are produced by the action of phosphoric anhydride on phenylpropionic acid; as the whole behaviour of the hydrocarbon pointed to its having a high molecular weight, it seemed probable that its formation was brought about by the condensation of two or more molecules of some intermediate product, possibly hydrindone. As this assumption could only be satisfactorily settled by preparing the hydrocarbon from hydrindone, attempts were made to synthesise the latter by treating phenylpropionic chloride with aluminium chloride; a few trials had already been made, with but slight success, when the writer's attention was called to a note by Hughes (*Proc. Chem. Soc.*, 96, 70), in which similar experiments with phenylpropionic chloride, carried out at Marsh's suggestion, were described; on continuing the experiments, it was soon found that, although Hughes failed to obtain hydrindone, it can be easily prepared in large quantities by the method suggested, and that, under suitable conditions, the yield of pure compound is 50—60 per cent of the theoretical, its formation being expressed by the equation—



The ketone prepared in this way crystallises in colourless waxy plates melting at 41—42°, and is identical with the hydrindone obtained by Gabriel and Hausmann (*Ber.*, xxii., 2019) from ethylic orthocyanobenzylacetate, and by König ("Inaug. Diss." Leipzig, 1889) from orthocarboxyhydrocinnamic acid.

Several derivatives of hydrindone have been prepared and characterised:—The hydrazone, $C_{15}H_{14}N_2$, crystallises from dilute alcohol in almost colourless needles melting at 127—128°. The *hydroxime*, $C_9H_8 \cdot NOH$, crystallises from benzene in colourless needles melting at 140—141°. The *nitro*-derivative, $C_9H_7O \cdot NO_2$, is a colourless crystalline substance melting at 75—76°.

When heated with moderately concentrated sulphuric acid, hydrindone yields a compound of the composition $C_{18}H_{14}O$; this condensation product crystallises from dilute alcohol in yellowish plates melting at 141.5—142.5°. When warmed with phosphoric anhydride, hydrindone is converted into a yellowish crystalline substance, which, judging from its general behaviour, is identical with the hydrocarbon obtained by treating phenylpropionic acid with phosphoric anhydride.

The investigation is being continued in other directions, as it appears probable that similar intramolecular condensations may be brought about in the case of other benzenoid compounds containing a side chain with the aid of aluminium chloride.

88. "The Re-resolution of Methoxysuccinic Acid into Its Optically Active Components." By T. PURDIE, Ph.D., B.Sc., and W. MARSHALL, B.Sc.

The authors find that inactive methoxysuccinic acid—prepared from fumaric acid by the addition of the elements of methylic alcohol—can be resolved into optically active components by means of the acid cinchonine salt, the salt of the dextrogyrate acid being less soluble in water and crystallising more readily than the corresponding salt of the lævogyrate acid. The separation of

the active acids effected in this manner, however, was only partial, the metallic salts obtained after removal of the cinchonine being mixtures of active with more or less inactive salt, from which the latter had to be separated by fractional precipitation or crystallisation.

In the first series of experiments the elimination of the inactive salt was effected by means of the different solubilities of the calcium and hydrogen potassium salts, the salts of the active acids being more soluble than those of the inactive acid. When solutions containing equal quantities of the oppositely active hydrogen potassium salts were mixed, the inactive salt was instantaneously precipitated.

The specific rotatory power of the active acids in a 5 to 10 per cent aqueous solution is about 33° ; they melt at 88° – 90° , the inactive acid melting at 108° . The specific rotatory power of the normal ammonium and potassium salts is of the same sign as that of the acids, but not so great, and it does not vary much with change of concentration; that of the calcium and barium salts is of opposite sign to that of the acid, and diminishes rapidly with decreasing concentration, the sign of the rotation of the latter salt being reversed in very dilute solutions.

89. "Optically Active Ethoxysuccinic Acid." By T. PURDIE, Ph.D., B.Sc., and I. WALLACE WALKER, M.A.

When spores of *Penicillium glaucum* are sown in a solution of the inactive acid ammonium salt of the inactive ethoxysuccinic acid formed by the addition of the elements of ethylic alcohol to fumaric acid, to which nutritive mineral salts have been added, an abundant growth of mycelium ensues, the result being that the leavogyrate component of the inactive acid is consumed, the dextrogyrate being left unaltered. The specific rotatory power of the acid in a 5 to 10 per cent solution is about $+33^\circ$; it melts at 76° – 80° , while the inactive acid melts at 86° .

The active acid ammonium salt crystallises with one molecular proportion, the corresponding inactive salt with half a molecular proportion, of water.

The inactive acid can also be resolved into its active components by means of the cinchonidine salt, the salt of the dextroethoxysuccinic acid being less soluble in water than its oppositely active isomeride. The active components were not obtained in the pure state by this process, but oppositely active acid ammonium salts were obtained which crystallise exactly like the salt produced by means of *Penicillium*, and whose specific rotations approximated in amount to that of the latter.

The authors find a close parallelism in respect of optical activity between the dextromethoxysuccinates, and dextroethoxysuccinates, the remarks about the former in the preceding abstract applying in general to the latter. The ethoxysuccinates are, however, more dextrorotatory or less levorotatory than the corresponding methoxysuccinates.

The bearing of some of these observations on the theories advanced by P. A. Guye (*Annalen* [6], xxv., 145) and by Crum Brown (*Proc. R. S. E.*, xvii., 181) regarding the relations of optical activity to the nature of the radicles which are united to the asymmetric carbon atom is discussed.

90. "The Formation of Benzylidihydroxypyridine from Benzylglutaconic Acid." By S. RUHEMANN, Ph.D., M.A.

Ethylic benzylglutaconate (*cf. Annalen*, ccxxii., 261) slowly dissolves in a concentrated aqueous solution of ammonia at 100° , forming a coloured liquid, from which acids precipitate benzylidihydroxypyridine,—a substance which exhibits both acid and basic properties. It crystallises in glittering plates which melt at 184° ; its dibenzoate melts at 164° . On oxidation, it readily yields coloured products possessed of tinctorial powers.

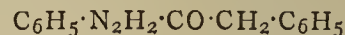
91. "The Action of Nitrous Acid on 1- α -amido-2- β -naphthol: a Correction." By R. MELDOLA, F.R.S.

In a paper published conjointly with G. T. Morgan (*Chem. Soc. Trans.*, lv., 114), wherein we had occasion

to identify α -amido β -naphthol in the presence of other bases, we stated that the yellow crystalline substance obtained by the action of nitrous acid was nitroso- β -naphthol. At the beginning of the present year a paper by Grandmougin and Michel appeared (*Ber.*, xxv., 972), in which these authors stated that the compound in question was β -naphthaquinone. I repeated the experiment at the time, and confirmed their statement. They have called attention to the discrepancy in another paper just to hand (*Ber.*, xxv., 3429), and ask for further details. In reply, I have only to state that I was not particularly concerned at the time with the nature of the crystalline compound, and it was not very closely investigated, as will be seen on reference to our paper (*loc. cit.*, p. 120). The superficial examination of the substance which we made led us to the belief that it was nitroso- β -naphthol, as it had a similar melting-point, and was soluble in alkali, and the subject was not further pursued, as it was beyond the scope of our investigation. The subsequent investigations by Grandmougin and Michel have convinced me that the substance which we had in hand was impure β -naphthaquinone, possibly mixed with some β -naphthaquinoneanilide, owing to the retention of a trace of aniline salt. The formation of β -naphthaquinone by the action of nitrous acid on α -amido- β -naphthol is a most unexpected discovery, which could not possibly have been foreseen, and the credit of which is entirely due to these authors. I have frequently had occasion to repeat this test in the course of some recent investigations, of which the results will be communicated to the Society subsequently: the method described by Grandmougin and Michel is certainly the simplest and by far the most effective yet made known for preparing pure β -naphthaquinone in large quantities.

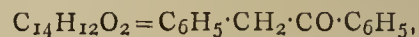
92. "Note on the Action of Phenylhydrazine on Mono- and Di-carboxylic Acids at Elevated Temperatures." By W. R. HODGKINSON and A. H. COOTE.

Phenylacetic acid and phenylhydrazine readily interact when heated together at 120° , forming—



(Rülow, *Annalen*, ccxxxvi., 196). In preparing this and similar hydrazides for another investigation, it was observed that a certain amount of decomposition took place, ammonia being one of the products. The course of the decomposition in the case of several monobasic benzenoid acids was, therefore, studied.

When heated with an equivalent quantity of phenylhydrazine, phenylacetic acid at first gives off water at temperatures up to 150° , the action then becomes more energetic, nitrogen and ammonia being evolved, light oils distilling over; and as the temperature is raised between 280° and 350° , a thicker oil distils over, a slight tarry residue being left in the retort. The lighter oils were found to consist of benzene and aniline. The greater portion of the heavy oil boiled between 320° and 370° C. On fractionating, a heavy substance was obtained boiling at about 340° free from nitrogen, which on analysis gave figures corresponding to the formula—



viz., 85.8 per cent carbon and 6.22 per cent hydrogen, the theoretical values being 86.0 and 6.12.

The decomposition cannot be very directly formulated. The first stage is the formation of the hydrazide—



but on heating this, $\text{NH}\cdot\text{NH}$ is split off, which immediately breaks up and reduces neighbouring molecules of phenylhydrazine partly to aniline and partly to benzene, with liberation of nitrogen and ammonia.

In the case of orthotoluic acid, $\text{C}_6\text{H}_4\cdot\text{CH}_3\cdot\text{COOH}$, a similar action takes place, but the amount of high boiling oil (ketone) is somewhat less, and the amounts of benzene and aniline somewhat greater.

In the case of phenylpropionic acid action also takes

place in a manner analogous to that observed in the case of phenylacetic acid.

Some dibasic acids, for example, succinic acid, exhibit a behaviour similar to that described when heated with phenylhydrazine, ammonia and nitrogen escaping, while a high boiling oil, free from nitrogen, distils over.

The authors desire to reserve the further study of these interactions for a short time.

Kopp Memorial Lecture.

An extra meeting of the Society will be held on February 20, 1893, at 8 p.m., the anniversary of the death of Hermann Kopp, when a lecture will be delivered by Professor Thorpe, F.R.S.

CORRESPONDENCE.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—When Mr. Wm. Thomson states that a constant majority of the Council of the Institute of Chemistry has consisted of Fellows more interested in teaching than in the practice of consulting and analytical chemistry, it appears to me that he states what is not a fact, and publishes as widely as he possibly can that which is very misleading. I would, therefore, beg all those who have received his circulars to examine the *List of Officers and Council* printed in the Register for 1892 and judge for themselves.

Of those who are professors, lecturers, or teachers, I can count but eight out of a total number of twenty-seven ordinary members of Council. Even if we take into account the president, vice-presidents, and treasurer, only twelve out of the thirty-five individuals can be supposed to belong to the class to which Mr. Thomson refers.

"It seems curious, therefore, that the Council of the Institute should be composed chiefly of those who do not belong to the class of members (by far the largest) for whose benefit the Institute was specially founded." (See Mr. Thomson's letter, CHEMICAL NEWS, vol. lxvii., p. 23.)

If it were so it would be *very curious*!—I am, &c.,

W. N. HARTLEY.

January 14, 1892.

POISONING BY AsH_3 .

To the Editor of the Chemical News.

SIR,—As the cases of poisoning by this gas are rare, I beg leave to draw your attention to the first which has occurred in this country. The victim was the Professor of Chemistry and Mineralogy in the University of Chile (Santiago)—Dr. Hans Oscar Schulze—who for the last ten years had been engaged in the study of the conditions under which bodies take the colloidal state, having already succeeded in obtaining in this form the trisulphide of antimony.

On the 18th November (1892), he was occupied in the laboratory of the University in making a current of AsH_3 pass through a solution of As_2O_3 , with the purpose of obtaining arsenic in a soluble form. It seems that the gas-generating apparatus was not hermetically closed, and let escape hydric arsenide in so small a quantity that its odour was not noticed by Prof. Schulze. One hour and a half after having commenced the operation this gentleman felt sick, and realised that he was poisoned by the AsH_3 . He left the laboratory, but before doing so wrote in chalk by the side of the apparatus, "Cuidado, AsH_3 !" (take care!).

Five days afterwards he was dead,—all efforts having proved useless to counteract the action of the poison.

Nothing could arrest the progress of the uræmia and the rapid destruction of the red corpuscles (the number of which decreased to 1,800,000 per cubic millimetre), and the fatty degeneration of the tissues.

Prof. Schulze had studied in Freiberg and in Leipzig; his numerous and important papers on chemistry and mineralogy have been published in the scientific periodicals of his country, Germany.—I am, &c.,

Q. NEWMAN.

Valparaiso, Laboratory of Chemistry,
Naval School, December 8, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 1, January 2, 1893.

This number contains no chemical matter.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. vii. and viii., No. 24.

Determination of the Acidity due to the Fixed and the Volatile Acids of Wine.—J. A. Müller.—The determinations of potassium bitartrate of tartaric acid, succinic acid, and tannin being effected, the acidity of the fixed acids enables us to find the quantity of the other acids such as the malic, or of acid salts which may be present. On the other hand, the standard of the volatile acids shows whether the wine examined is sound or diseased. He takes first the total acidity in 10 c.c. by means of a standard baryta-water, 1 c.c. of which corresponds to 0.01 grm. of sulphuric acid, using as indicator an alcoholic solution of phenolphthaleine at 5 grms. per litre; 10 c.c. of the wine are then put in a flask containing about 100 c.c., the neck of which is connected to a water-sprengel. A vacuum is made and maintained for ten minutes, agitating briskly towards the end to facilitate the expulsion of the last fractions of the dissolved gases. The total acidity is again determined. To find the acidity due to the fixed acids and to their acid salts, M. Müller evaporates 10 c.c. of the wine in a porcelain capsule of 12 c.m. in diameter and having a round bottom. The evaporation is made over a small Bunsen flame, holding the capsule by the spout. A rotatory movement is given to the liquid, and the surface is blown upon from time to time to eliminate the vapours. The evaporation lasts only a few minutes, and the residue is dried for two to three minutes, taking care not to heat the capsule to such a degree that it becomes painful to the hand. If there are any brown specks in the residue the heat has been excessive. The residue is then dissolved in distilled water and the acidity is determined again. The difference between the second and the third determination shows the volatile acids. The difference between the first and the second is due to CO_2 .

Contributions to Kjeldahl's Process for the Determination of Nitrogen.—Carl Arnold and Konrad Wedemeyer.—The authors examine in succession the action of different oxidising agents; the behaviour of substances which contain nitrogen in ring-formed combination; the behaviour of compounds which contain groups connected by atoms of nitrogen; the behaviour of some other nitrogen compounds; comparative determinations of nitrogen in compounds where it is present as oxides, and new methods for determining the oxides of nitrogen.—*Zeit. für Anal. Chemie*, xxxi., Part 5.

MEETINGS FOR THE WEEK.

- MONDAY, 23rd.—Medical, 8.30.
 TUESDAY, 24th.—Institute of Civil Engineers, 8.
 ——— Royal Medical and Chirurgical, 8.30.
 ——— Photographic, 8.
 ——— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psychophysiology," by Prof. Victor Horsley, F.R.S.
 ——— Society of Arts, 8. "The Theory of 'Storiation' in Art," by Hugh Stannus, F.R.I.B.A.
 WEDNESDAY, 25th.—Society of Arts, 8. "The Fine Arts in Relation to the Sanitary Condition of our Great Cities," by Wyke Bayliss, P.R.S. Brit. Arts.
 ——— British Astronomical Association, 5.
 ——— Geological, 8.
 THURSDAY, 26th.—Royal, 4.30.
 ——— Royal Institution, 3. "Tennyson," by the Rev. Canon Ainger, M.A., LL.D.
 ——— Institute of Electrical Engineers, 8.
 FRIDAY, 27th.—Royal Institution, 9. "The Just-Perceptible Difference," by Francis Galton, F.R.S.
 ——— Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.
 ——— Physical, 5. "Japanese Magic Mirrors," by S. P. Thompson, F.R.S. "The Perception of Colour," by W. F. Stanley, F.G.S. "Recent Determinations of Molecular Refraction and Dispersion," by Dr. J. H. Gladstone, F.R.S.
 SATURDAY, 28th.—Royal Institution, 3. "Expression and Design in Music," by Prof. C. Hubert H. Parry, M.A.

TO CORRESPONDENTS.

W. Rushby.—(1) Prof. Mallet's Address on the Life and Work of Stas will be published in the CHEMICAL NEWS in the course of a few months. (2) See the CHEMICAL NEWS, vol. lxiv., p. 108. (3) *Proc. R. S.* (4) It publishes a monthly journal.

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The following appendix has been written upon the same lines as in former editions, save that it has been enlarged, and in reality now constitutes a treatise on the chemical substances occurring in the animal body. As in former editions it is entirely the work of Dr. A. Sheridan Lea. The references given, though extensive, are not intended to be exhaustive. An effort has been made to make the references to recent works as complete as possible, other references are to papers, which themselves give full references, and will therefore serve as a guide to literature of the subject; and some have been inserted in order to inform the student of the dates at which important results were first described."—From the Preface.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1731.

THE RATE OF EXPLOSION IN GASES.*

By HAROLD B. DIXON, M.A., F.R.S.,
Professor of Chemistry in the Owens College, Manchester.

1. BERTHELOT'S measurements of the rates of explosion of a number of gaseous mixtures have been confirmed. The rate of the explosion wave for each mixture is constant. It is independent of the diameter of the tube above a certain limit.

2. The rate is not absolutely independent of the initial temperature and pressure of the gases. With rise of temperature the rate falls; with rise of pressure the rate increases; but above a certain *critical pressure* variations in pressure appear to have no effect.

3. In the explosion of carbonic oxide and oxygen in a long tube, the presence of steam has a marked effect on the rate. From measurements of the rate of explosion with different quantities of steam, the conclusion is drawn that at the high temperature of the explosion wave, as well as in ordinary combustion, the oxidation of the carbonic oxide is effected by the interaction of the steam.

4. Inert gases are found to retard the explosion wave according to their volume and density. Within wide limits an excess of one of the combustible gases has the same retarding effect as an inert gas (of the same volume and density) which can take no part in the reaction.

5. Measurements of the rate of explosion can be employed for determining the course of some chemical changes.

In the explosion of a volatile carbon compound with oxygen, the gaseous carbon appears to burn first to carbonic oxide, and afterwards, if oxygen is present in excess, the carbonic oxide first formed burns to carbonic acid.

6. The theory proposed by Berthelot—that, in the explosion wave the flame travels at the mean velocity of the products of combustion—although in agreement with the rates observed in a certain number of cases, does not account for the velocities found in other gaseous mixtures.

7. It seems probable that in the explosion wave—

- (1) The gases are heated at *constant volume*, and not at *constant pressure*;
- (2) Each layer of gas is raised in temperature *before* being burnt;
- (3) The wave is propagated not only by the movements of the burnt molecules, but also by those of the heated but yet unburnt molecules;
- (4) When the permanent volume of the gases is changed in the chemical reaction, an alteration of temperature is thereby caused which affects the velocity of the wave.

8. In a gas, of the mean density and temperature calculated on these assumptions, a sound wave would travel at a velocity which nearly agrees with the observed rate of explosion in those cases where the products of combustion are perfect gases.

9. With mixtures in which steam is formed, the rate of explosion falls below the calculated rate of the sound wave. But when such mixtures are largely diluted with an inert gas, the calculated and found velocities coincide. It seems reasonable to suppose that at the higher temperatures the lowering of the rate of explosion is brought about by the dissociation of the steam, or by an increase in its specific heat, or by both these causes.

10. The propagation of the explosion wave in gases must be accompanied by a very high pressure lasting for a very short time. The experiments of MM. Mallard and Le Chatelier, as well as the author's, show the presence of these fugitive pressures. It is possible that data for calculating the pressures produced may be derived from a knowledge of the densities of the unburnt gases and of their rates of explosion.

ON A NEW BOILING AND DISTILLING VESSEL.*

By THEOD. FREDERKING.

AN invention has lately been made in Germany which is likely to become of great importance for the whole chemical industry, for breweries, for manufacturers of food-stuffs, &c. This invention, which has been patented in all countries, relates to a boiling vessel which does not come into contact with the fire, and in which any combustible, explosive, and similar matter, may be boiled, vaporised, melted, or distilled, which requires to be boiled at a precisely fixed temperature, and which possesses a high boiling or melting point.

The peculiarity of the vessel is, that pipes of great strength are cast into its massive metal walls, so that the heat introduced into the pipes is rapidly communicated to the good conducting wall and to the contents of the vessel. The pipes may be so thick-walled (for instance, Perkin's pipes) as to bear any required pressure, the walls of the vessel being consequently entirely free from the pressure of the heating medium. By these means, the steam pressure, instead of being limited to three atmospheres, as formerly, may be increased to any degree without danger, so that, for instance, with an additional pressure in the steam boiler of six, eight, or ten atmospheres, a boiling temperature of 150°, 160°, or 180° C. may be obtained.

Higher temperatures than those which can be obtained by steam are reached in a simple way by hot-water heating. For this purpose an apparatus of Perkin's or other similar pipes, situated in a suitable stove, is connected with the pipes in the walls of the vessel into a closed pipe system. Distilled or condensation water filled into the pipes will circulate through the pipe system, taking up heat in the stove and transmitting it to the massive walls of the vessel and to the contents of the latter. As water cannot evaporate in a closed conduit, a temperature of from 350° to 400° C. can be reached easily and without inconvenience. These boiling arrangements, being neither steam nor hot water, are not subject to governmental supervision, for as the strength of the pipes is tried up to 300 atmospheres, and as they contain but a small quantity of water, as moreover the walls of the vessel are free from pressure, and as the stove may be erected at any distance from the boiling vessel, there is no danger in working.

As may be foreseen, the vessel worked by steam should be quickly adopted in breweries for the coppers, because the great losses of fuel, as well as of the copper burning through when they are heated over fire, make the introduction of steam boiling very desirable, and because the deficiencies connected with the former way of boiling by steam in double walled vessels with a low steam pressure are entirely done away with. Moreover, the boiling of pitch is also advantageously effected with patent vessels and water heating, on account of the former's great danger of fire. As the stove may be placed in any side room, danger of fire in the pitch-boiling house will be out of question.

The steam boiling vessels are also employed with advantage for the melting of tallow or grease; the requi-

* Abstract of the Bakerian Lecture read before the Royal Society, January 19, 1893.

site temperature of about 160° to 170° being easily obtained through steam of eight or ten atmospheres additional pressure introduced into the walls of the vessel. By the employment of a steam boiler, specially erected for the melting, the working may be arranged to be very profitable.

The patent vessels with hot water arrangement are of great importance—for instance, for the manufacturing of printer's inks, oil cloth, &c., for the boiling of linseed oil, and for all industries working with resins, pitch, tar, distillation of coal, &c. These few examples are sufficient to show what important part the new boiling vessel is to play in industry, and we will only still mention the melting of sulphur (which may be effected in the patent vessel with steam at four atmospheres additional pressure, without danger and in less time than over fire), the manufacture of soap and candles, perfumery, essential oils, colours (for instance, boiling vessel constructed as autoclaves), and the dye-works. At the same time, conscious that this does not by any means exhaust the availableness of the apparatus, we may even say that it will soon be adopted in all industries where boiling, vaporising, melting, or distilling is done.

ON THE PROBABLE SPECTRUM OF SULPHUR.

By JOSEPH SWEETMAN AMES.

WHILE pursuing in the winter of 1889 some investigations on the spectrum of hydrogen, I was surprised to find on several of my photographic plates lines which evidently had no connection with hydrogen. These lines formed most beautiful series, bearing a striking resemblance to the B group of the solar spectrum. In some cases the series overlap, in others they are perfectly distinct. The head of each series is towards the shorter wave-lengths, and the lines are generally grouped in pairs. There is one very faint series of pairs beginning about wave-length 2860; at wave-length 3020 a series of single lines begins; from wave-length 3065 to wave-length 3200 there is almost hopeless confusion of overlapping series, most of the lines being strong and sharp; and at wave-length 3200 begins a series of at least twelve pairs, which in its intensity and in all its physical properties is remarkably like the B group.

My reason for believing these series to belong to the spectrum of sulphur are largely negative ones. The plates on which they appeared were taken consecutively on the same day. Since then I have tried to secure the same or similar conditions; but not once have I found a trace of the lines. I was using vacuum tubes containing large aluminium electrodes; and the hydrogen was admitted to the tubes over a mercury trap. Plugs of sulphur, blocked by glass wool, were interposed in the connecting tubes to stop the mercury vapour. It sometimes happened that the hydrogen would bubble up through the mercury trap faster than was desirable; and it is perfectly possible that with the mercury vapour, traces of which could always be detected in my tubes, some particles of sulphur were carried through. The only impurity detected in my tubes was mercury. Traces of water vapour always linger on the walls of vacuum tubes, but its spectrum is known. I have compared these new lines with all the spectra at my disposal, and can find no agreement. The fact that these lines form series so wonderfully like the B group, which is due to oxygen, is an argument, however faint, that they may belong to sulphur, since oxygen and sulphur are so closely connected chemically.

Being unable to convince myself that the spectrum which I obtained was really due to sulphur, I have never measured my plates carefully. I publish this note now only in the hope that some investigator may be able to succeed better

than I in securing the necessary conditions for repeating my observations.—*Astronomy and Astro-Physics*, January 1893.

SOME REMARKS ON THE EXAMINATION OF THE RARE GADOLINITE EARTHS, AND IN PARTICULAR ON DETERMINING THE EQUIVALENTS OF THESE EARTHS BY CONVERTING THE OXIDE INTO THE SULPHATE.

By GERHARD KRÜSS.

(Concluded from p. 33).

FOR the complete removal of the excess of sulphuric acid without the formation of basic sulphate, the crucible is placed above the flame, 3 c.m. in height, of an ordinary Bunsen burner, provided with a chimney so that the point of the flame is at the distance of 8 c.m. from the bottom of the crucible. After one hour the flame is raised to 8 c.m. After six hours the crucible is allowed to cool for one hour in the exsiccator and weighed. It is then heated again for six hours, again weighed, &c. The second weighing generally agrees with the former except for the slight increase of weight which takes place during weighing. If this is not the case with larger quantities, the third or fourth weighing proves constant.

In any case already in the third or fourth weighing, the scale should be loaded with the same weights used in the first weighing, or rather less, before the crucible with sulphate is removed from the phosphoric anhydride desiccator to the balance. The same procedure is also to be employed in taking the constant weight of the earths after repeated ignition.

A quantity of 0.2 gm. oxide is sufficient for an accurate result, and it is not advisable to use more than 0.5 gm. earth for determining the equivalent, as otherwise the sulphate formed can only be brought to a constant weight after a very long time. For the conversion of oxide into sulphate porcelain crucibles were preferred to those of platinum. Independently of the considerable number of crucibles requisite for the simultaneous performance of ten to fifteen analyses, the substance may be more easily heated *uniformly* to several hundred degrees in a porcelain crucible than in one of platinum, since platinum conducts away the heat more quickly from the hottest part of the bottom. It might be objected against the use of porcelain that during the conversion of the oxide into sulphate, by fuming off the free acid, the glaze of the crucible might be perhaps attacked, and thereby the weight of the crucible might vary during the experiment.

Only in single cases was the glaze of the crucible found distinctly corroded after being once used, which was accompanied by a considerable loss of weight of the crucible. In such case, not merely the determination in question, but the crucible itself was at once rejected. But if the weight of the crucible varied in the course of the first experiment only by $\frac{1}{10}$ or $\frac{2}{10}$ of a m.grm., the crucible could be used for an extensive series of determinations. In order to show the permanence of the crucibles used, the author gives the weights which some of them showed after repeated ignitions.

In order to show the stable nature of the crucibles employed, I append the weights of some of them after each ignition before a new determination. The numbers show sufficiently the suitableness of porcelain crucibles for the purpose in question.

The following data show, in opposition to the experiments of G. H. Bailey, that the rare earths may be quantitatively converted into sulphate whether they are strongly or feebly basic, and that in the process of driving off the excess of sulphuric acid, we can arrive at a point where the weight is constant. This may be seen from

the following results, which show the weights of crucible + earthy sulphates after repeated ignitions—each time for six hours—and weighing.

Erbium sulphates.			
Ytterbium sulphate.			Yttrium sulphate.
III R=172.03	III R=169.6	III R=165.43	III R=93.72
8.6494	7.6125	6.9538	6.2906
8.6496	7.6122	6.9536	6.2908
8.6496	7.6122	6.9537	6.2908
8.6495	7.6123	6.9536	6.2907
Didymium sulphates.			
III R=140.2	III R=145.17	III R=144.53	
7.8589	11.2735	13.2030	
7.8585	11.2731	13.2026	
7.8583	11.2735	13.2029	
7.8586	11.2723	13.2026	
	11.2725	13.2027	

The residual sulphates, in spite of the prolonged heating above the incipient boiling-point of sulphuric acid, did not give off any more acid. They also gave clear solutions in water. Hence, according to the accepted view, they were neutral sulphates. Still, it might be objected that a basic earthy sulphate may possibly be slightly soluble in a concentrated solution of neutral sulphate, and that the observation of the perfect solubility of the residue, after the ignition, does not justify the conclusion of the absence of basic salt.

If during the expulsion of the excessive sulphuric acid there has been formed in part a basic sulphate, it must seem strange that on further ignition to the same temperature this decomposition is suddenly arrested, whilst in such decompositions the weight of the substance approaches asymptotically to a constant limit value. But in this case the weight of the sulphate can by no means remain unchanged at two different temperatures. At a higher temperature the decomposition must certainly continue if the formation of a basic salt has begun at a lower temperature. The following experiments show the behaviour of the sulphates in this direction. The materials employed were:—

	No. 1. Yttria— almost white.	No. 2. Ytterbia— snow-white.	No. 3. Terbiferous yttria—yellow.
Weight of crucible =	7.4856	6.7979	8.1175
D. + oxide =	7.9153	7.3603	8.4007
Crucible + sulphate:—			
I. {	8.5282	7.613	8.6800
{	8.52	7.610	8.6779
{	8.48	7.6083	8.6768
II. {	8.3643	7.6066	8.6765
{	8.3615	7.6064	8.6758
{	8.361	7.6063	8.6757
{	8.3578	7.6061	8.6759
{	8.3578	7.6060	
{	8.3582		
III. {	8.3568	7.6059	8.6757
{	8.3572	7.6061	8.6755
{	8.3568	7.6060	8.6756
IV. {	8.3568	7.6060	
{	8.3570	7.6059	

The numbers under I. represent the weights of the crucibles + sulphates after each eight hours' heating on the iron plate with the triple burner. In II. each was heated for eight hours with a direct Bunsen flame 3.8 c.m. high (regulated with a precision cock), so that its point was at the distance of 8.6 c.m. from the bottom of the crucible. Neither lead nor tin fused so that the temperature was evidently below 228°, and yet, constancy was obtained for specimens 2 and 3.

In III. the crucibles were heated for eight hours with

a Bunsen flame 9 c.m. in height, the point of which was at the distance of 4 c.m. from the bottom of the crucible. Lead melted at this temperature, so that the heat was raised to 325° or higher. In IV. the flame, 11 c.m. in height, reached almost to the bottom of the crucible. Zinc, or antimony, did not melt at this temperature, so that it must have been below 415°. It may, approximately, have been from 370° to 380°. It must have been between 325° and 415°, and indeed considerably above the melting-point of lead (325°), as this had been already exceeded in III.

Except in experiment No. 1 the earthy sulphates had given off all free acid completely below 228°, even if only on prolonged heating. If we consider the sulphate of the feeblest base ytterbium sulphate (experiment No. 2), which must be most readily decomposed by heat, and which reached a constant weight even below 228°, after being heated for forty hours up to 380°, retained the same weight.

The determination of the equivalents of the gadolinite earths, by converting the oxide into anhydrous sulphate, can therefore be conducted with perfect exactitude if the fuming off the excess of free acid is cautiously effected by keeping the crucibles first at from 200° to 220°, and then gradually heating above 290°—the point at which sulphuric acid begins to boil—up to about 350°. In this manner we obtain neutral earthy sulphates free from uncombined sulphuric acid and from basic sulphates. If the conditions of the experiment are regulated by means of precision gas-cocks, the conversion of the earths into sulphates can be effected simultaneously in a great number of determinations without the necessity for unbroken attention. If the earthy sulphates are heated above the melting-point of antimony, the sulphate is gradually decomposed, with continuous loss of weight.

Finally, it must again be pointed out, that the excess of sulphuric acid must be driven off with the least possible interruption, and that the contents of the crucible must not be allowed to stand in moist air before the end of the operation. In such cases the salt tumefies, and on further heating is found in a state of much finer division, so that the crucible is more completely filled; the contents of the crucible cannot then be so uniformly heated as when smaller quantities of sulphate cover the bottom in the form of crusts.

In such a finely-divided and more unfavourable state was the yttria No. 1, mentioned in the above table. Hence this sulphate did not reach a constant weight until later. It is equally unfavourable to use more than 0.5 grm. of earth for the experiment, as a longer time is required before the weight becomes constant. According to the above example, 1.3073 grms. of a terbiferous yttria after conversion into sulphate, yielded exactly the same

III
R of 99.6 for this yttria material as 0.2832 grm. of the same oxide in another determination. Determinations of equivalents, with from 0.2 to 0.4 grm. of the earth in considerable time, and at the same time with equally distinct results.

The above method for determining the combining weights of the earths is perfectly unobjectionable under the conditions laid down. It was applied in this manner in the researches on erbium, holmium, and terbium (to be given below), as well as in new methods for separating the earths.

Before reporting the latter, I wish to insert a brief conspectus of the methods hitherto employed for separating and isolating the yttrium and cerium earths. The conspectus has been drawn up by Dr. A. Loose. In our more extensive inorganic text-books, and in some general collected works on chemistry, there may be found in part excellent monographs of the rare earths. But such a conspectus may now be made considerably more complete, especially as of late many researches have been made in this department. Perhaps the following conspectus, drawn up as briefly as possible, and characterised

by its modified arrangement, may be found to facilitate a view of previous researches in this direction, and to render references to the bibliography of the subject more easy.

THE CONSTITUTION OF MAGNETIC OXIDES.*

By STEPHEN H. EMMENS.

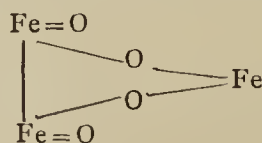
In the process of nickel manufacture practised by the Emmens Metal Company at Youngwood, Westmoreland Co., Pa., the metal is granulated by pouring it, when molten, into water. This operation usually proceeds quietly and without interruption; but occasionally sharp explosions take place as the metal touches the surface of the water. Investigation into the conditions of these explosions has shown that the phenomenon is always accompanied by a more or less oxidised state of the molten metal; that is to say, the nickel ore has not been completely reduced to metal in the operations preceding that of granulation.

It is also noticed that when no explosions occur, and when the molten metal sinks quietly to the bottom of the granulating vessel, bubbles of gas rise to the surface of the water and burn there with a blue flame.

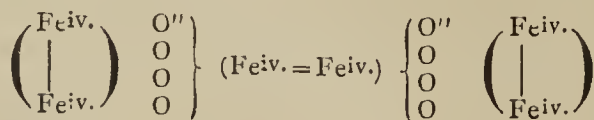
Inasmuch, then, as the fully reduced metal appears to decompose water, and as the partially reduced metal causes an explosion when coming into contact with water, it would seem that, in the latter case, the presumably homogeneous mass of molten metal consists partly of molecules of free nickel which liberate hydrogen from the water, and partly of molecules of nickel oxide which supply oxygen to at once combine explosively with the hydrogen.

This explanation, namely, that an oxide of nickel probably exists in which the metal is partly metallic and partly oxidised, suggests an analogous explanation of an analogous phenomenon, *i.e.*, the magnetic character of certain oxides.

Chemists have hitherto been, for the most part, agreed in considering the magnetic oxide of iron, Fe_3O_4 , as being, to quote Mendeleeff ("Principles of Chemistry," translated by Kamensky and Greenaway), "composed of ferrous and ferric oxides." Indeed, Mendeleeff specifically speaks of "the so called magnetic oxide containing atomic quantities of the suboxide and oxide, *viz.*, FeO , $\text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$." And the new edition of "Watts' Dictionary" says " Fe_3O_4 may be regarded as FeO , Fe_2O_3 "; while the old edition (Second Supplement) gives the following graphic formula for Fe_3O_4 :—



in which ferrous (bivalent) iron is represented as forming an unsaturated compound, FeO_2 , which is united with an unsaturated compound, Fe_2O_4 , of ferric (in this case quadrivalent) iron. Drechsel, on the other hand ("Introduction to the Study of Chemical Reactions," translated by Merrill), admits Fe_3O_4 , or rather Fe_6O_8 , to a place among the true iron oxides, and pictures its constitution as follows :—



contending that iron is quadrivalent only, and not at any time either bivalent or trivalent.

None of these views throw any light upon the most

remarkable property of Fe_3O_4 ; that is to say, they show no reason why it should be much more magnetic than its fellow oxides, and especially than the protoxide, FeO , which contains a larger percentage of the metal. The question, therefore, of the true molecular constitution of magnetic iron oxide may be regarded as being still an open one; unless, indeed, there be any considerations of paramount importance already advanced for compelling the recognition of $\text{FeO}, \text{Fe}_2\text{O}_3$. If we search for such reasons we shall find them to be two in number, *viz.* :—

1. *The Argument from Isomorphism.*—Magnetite (Fe_3O_4) is found in nature as a mineral isomorphous with spinel (MgAl_2O_4), gahnite (ZnAl_2O_4), zeilanite (FeAl_2O_4), franklinite (ZnFe_2O_4), and chromite (FeCr_2O_4). It is assumed that spinel must contain MgO , that gahnite and franklinite must contain ZnO , that zeilanite must contain Al_2O_3 , that chromite must contain Cr_2O_3 , and that therefore the former three must also contain Fe_2O_3 and the latter two FeO . But if these assumed necessities do not in point of fact exist, the argument falls to the ground; and as no attempt is made to prove their existence we are justified in treating the argument as of no weight,—a very frequent thing in cases of isomorphism.

2. *The Argument from Solution.*—If Fe_3O_4 be dissolved by acids, ferrous and ferric salts are found in solution. This is held as proof that Fe_3O_4 consists of FeO and Fe_2O_3 . But if Fe be dissolved by H_2SO_4 and form FeSO_4, Aq , no one dreams of declaring that Fe must have contained FeO . Solution certainly implies a degree of molecular disaggregation that admits of re-arrangement; and so far from the presumption being in favour of a continuance of pre-existing molecular structure, it is obviously the reverse.

Seeing, then, that no good reason exists for regarding Fe_3O_4 as $\text{FeO}, \text{Fe}_2\text{O}_3$, it may be well to enquire whether any valid arguments can be advanced against such a view.

First, the compound Fe_2O_3 is of a very stable character, and is, with reason, regarded as "saturated." If, then, it be linked to FeO , this can only be by means of some hitherto unknown and unrecognised affinity invented or imagined for the occasion.

Secondly, FeO is of a very unstable character; so much so, indeed, that the ordinary assumption of its being "saturated" appears to have very slender foundation. Its combinations with Fe_2O_3 by means of the mysterious affinity above mentioned should not, apparently, interfere with its proneness to oxidation; and the compound $\text{FeO}, \text{Fe}_2\text{O}_3$ should readily change into $2\text{Fe}_2\text{O}_3$, whereas, in point of fact, Fe_3O_4 is so stable and unoxidisable that it is artificially produced on the surface of iron (*i.e.*, the "Barff" and "Bower" processes) as a durable coating for the purpose of preventing that metal from rusting.

Thirdly, FeO is somewhat magnetic, but Fe_2O_3 is very slightly so, if at all. According to Becquerel, Fe_2O_3 is diamagnetic, and this is also stated by Mendeleeff and other authorities; though Plucker gives the specific magnetism of specular iron ore as 533 compared with 4027 for Fe_3O_4 , and Sidot (*Compt. Rend.*, lxvii., 175) has obtained an oxide exhibiting magnetic polarity by heating ferric oxide in an earthen tube placed in the magnetic meridian to a temperature not sufficient to fuse the oxide. A. Frenzel also (*Jahr. f. Min.*, 1874, 685) obtained small rhombohedrons of iron glance, slightly magnetic, by igniting a precipitate of ferric hydrate; and Malaguti (*Ann. Chim. Phys.*, [3], lxi., 214) states that a magnetic variety of Fe_2O_3 exists. These discrepant assertions may perhaps be caused by the fact that Fe_2O_3 when strongly heated gives off oxygen, and is partially converted into Fe_3O_4 . But be this as it may, the very slightly magnetic character of both FeO and Fe_2O_3 is as incontestable as is the highly magnetic character of Fe_3O_4 . And as magnetism is conceded to be a physical property, dependent in some unknown way upon the molecular structure of bodies, the inference is irresistible that the molecules of iron and oxygen in Fe_3O_4 cannot be arranged

* *Journal of Analytical and Applied Chemistry*, October, 1892.

in two groups, one of which has the structure of FeO and the other that of Fe₂O₃.

Fourthly, neither the hydrate of FeO nor that of Fe₂O₃ is magnetic. But the hydrate of Fe₃O₄ is attractable by the magnet, both when in the liquid from which it is precipitated and when in a dry state. Here, again, it seems idle to suppose that Fe₃O₄ exists as a combination of FeO and Fe₂O₃.

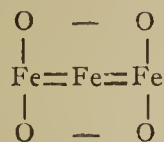
Fifthly, Lefort (*Compt. Rend.*, lxi., 179) has succeeded in forming a definite salt by dissolving Fe₃O₄ in H₂SO₄, and evaporating the solution over H₂SO₄. This sulphate has the composition Fe₃O₄.6SO₃.15H₂O. But FeO combines with one molecule of SO₃ and Fe₂O₃ with three molecules of SO₃; so that the mixture FeO + Fe₂O₃ will combine with 4SO₃. The combining power of Fe₃O₄ is therefore very different from that of FeO, Fe₂O₃.

Sixthly, if Fe₃O₄ be composed of a molecule of FeO united to one of Fe₂O₃, it would seem that only one grouping is possible, and that no isomer of the normal Fe₃O₄ can exist. But according to Moissan (*Ann. Chim. Phys.*, [5], xxi., 223) and Berthelot (*Ann. Chim. Phys.*, [5], xxiii., 118), two varieties of Fe₃O₄ exist, having distinct specific gravities, different solubilities in HNO₃, and different behaviours when exposed to heat. It follows that Fe₃O₄ cannot have the constitution FeO, Fe₂O₃; unless, indeed, the isomerism be regarded as due to the presence of two varieties of Fe₂O₃.

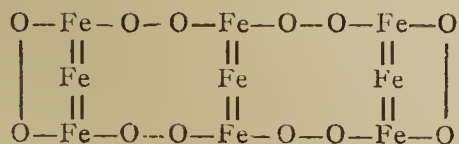
Having now shown that no good reason exists for regarding Fe₃O₄ as being FeO, Fe₂O₃, and that many good reasons exist against such a view, it remains for me to point out that another view of the molecular constitution is possible and preferable.

Let us, with Drechsel, F. W. Clarke, and some other chemists, regard iron as being a quadrivalent element, and let us dismiss the imaginary *ferrosium* and *ferricum* from our minds. Let us also consider oxygen as being virtually bivalent. And let us recognise the fact of the magnetic property of iron being impaired and well nigh destroyed by the union of the metal with oxygen; a fact which leads us to conclude that in any strongly magnetic oxide of iron some part at least of the metallic molecules must exist uncombined save with iron. The problem then arises whether any possible grouping of the molecules in Fe₃O₄ can comply with the requirements thus premised.

I submit that the following graphic formula is a solution of the problem, viz:—

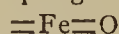


Here each molecule of Fe is quadrivalent, and each molecule of O is bivalent. One-third of the iron, moreover, is uncombined save with iron, and is, therefore, fully magnetic. We also see that a polymeric form is possible, viz:—

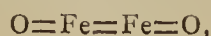


and this may well account for there being two varieties of magnetic oxide, in both of which the proportions of iron and oxygen are as Fe₃ to O₄.

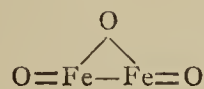
The slightly magnetic character of the protoxide may, I think, be shown by adopting the following formula:—



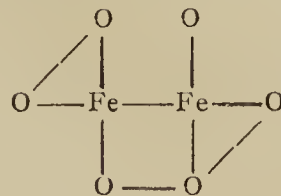
in which the iron molecule is not fully linked, and is, therefore, free to combine with another molecule of FeO, thus,—



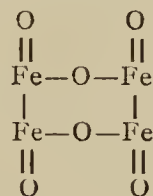
forming a somewhat magnetic body, which is easily oxidised into the less magnetic ferric oxide, Fe₂O₃,—



and this, by further oxidation, becomes ferric anhydride, Fe₂O₃, or Fe₂O₆—



It will be observed that the suggested constitution of Fe₂O₃ also admits of a polymeric variation, viz:—



and in accordance with this view it may be mentioned that two varieties of ferric oxide as well as of Fe₃O₄ are known. Indeed, as Mendeleeff very justly observes (*loc. cit.*, p. 324), "all phenomena observed respecting ferric oxide (colloidal properties, various forms, formation of double basic salts) demonstrate that this substance, like silica, alumina, lead hydroxide, &c., is polymerised, that the composition is represented by (Fe₂O₃)_n."

In conclusion I would add that in the foregoing observations I have employed the concepts of molecule, valency, and the like merely as customary useful aids to such an understanding and explanation of chemical and physical relations and phenomena as is possible in the present limited condition of our knowledge, and not as representing the esoteric facts of nature.

CHEMICAL ACTION BETWEEN SOLIDS.*

By WILLIAM HALLOCK.

In a note on a new method of forming alloys published some time ago (W. Hallock, *Zeit. Phys. Chem.*, ii., 1888, p. 6; *Science*, xi., 1888, p. 265), I suggested some additional experiments which I intended to make, and I now give the results thus far obtained. Unfortunately, other work prevents my continuing the investigation at present.

Inasmuch as the method and principle† seemed well established where metals were used to produce alloys, an attempt was made to include some chemical reactions in the list. The most natural cases were the freezing mixtures where solid reagents are used. In order to surely have both constituents in a decidedly solid state, the experiments were performed in a vessel cooled to a temperature of -10° or 12° C., care being always taken to leave the reagents in the vessel long enough for them to assume a temperature decidedly below zero Centigrade. Under these conditions a crystal of rock salt (NaCl) and a piece of clean, dry ice, were gently brought in contact, lying side by side on a watch-glass. Of course the result

* This paper was read in part before the Phil. Soc. of Washington, D.C., Oct. 13, 1888, and appeared in full in the *Amer. Jour. Sci.*, vol. xxxvii., 1889, p. 402.

† O. Lehmann (*Wiedemann Ann.*, xxiv., 1885, p. 5), suggested the theoretical possibility of producing an alloy in this way. I had overlooked his paper until recently. Mr. Lehmann, however, evidently did not consider it possible to fulfil the necessary conditions and did not try the experiment.

was the solution of salt, but old as this experiment may be, it appears here in a new connection, as an example of the union of two solids below the melting-point of either, but above that of the product. The piece of ice was frozen to the glass, and during the operation the crystal was drawn several millimetres across the glass, doubtless by capillarity, as the solution ran out at the bottom of the surface of contact as fast as it formed, the attraction being sufficient to move a crystal several grms. in weight.

Similar experiments were performed with sodium and potassium, nitrate potassium, calcium and ammonium chloride, and sodium and potassium hydrate, with a similar result in all cases. These are all well-known results, but wherein do they differ from the new method of forming alloys? This question suggests another. Are the metals combining to form an alloy in the new way a freezing mixture? A thorough investigation of the question would require more complicated experiments than I had time to perform. One test, however, is very simple, that with potassium and sodium.

Into a small porcelain crucible weighing 15 grms. and containing about an equal weight of petroleum, were placed pieces of the two metals, about 3 grms. of each. One junction of a thermo-element was forced into the piece of potassium and gave its temperature accurately. After the whole had assumed the room temperature, clean faces of the two metals were brought into contact, the liquefaction began, and *the temperature immediately fell*. It required about two hours to complete the liquefaction, and about one and a half hours to attain the minimum of temperature. No precautions were taken to prevent the calorimeter taking up heat from its surroundings, and no doubt, it absorbed considerably in the long time, and yet the maximum fall in temperature amounted to 2.4°C .—very large considering the small weight of the reagents compared with the calorimeter. Thus it appears that sodium and potassium are, under such circumstances, a "freezing mixture," and analogy at least would lead one to believe that other alloys also absorb heat in their formation; but future experiment must decide the point.

In the cool vessel above described, a piece of sodium or potassium was placed upon a piece of dry ice; almost instantly the reaction commenced and proceeded vigorously. It is, however, scarcely safe to consider this a case of chemical action between solids, because the reaction is probably as follows: The vapour from the ice attacks the metal, forming the hydrate which unites with other ice, forming a solution, which is then further acted upon by the metal, and in the whole process heat is generated sufficient to raise the temperature of the reagents very considerably. Perhaps in the other freezing mixtures, ice and salt, &c., it is the vapour of the water or ice which initiates the reaction.

In view of these and other considerations, the idea is evident that perhaps many substances have a slight vapour tension at temperatures considerably below their melting-points, and are surrounded by a thin atmosphere of their own vapour over their clean surfaces, and it is only necessary to bring two such atmospheres to interpenetration in order to initiate the reaction which will then continue, provided the product (liquid or gas) escapes easily and does not clog the operation. In very many cases substances are found to give off a vapour below their melting-point, and it is natural to suppose that there is a film of that vapour over the surface of the body, as there is a layer of saturated air over water. The mechanical theory of the composition of matter lends plausibility to the above suggestion. If these considerations are correct they foretell the regelation of substances like camphor and ice, without any pressure whatever. That loose pieces of camphor will become welded together by simple contact is well known. The operation appears to me thus:—In an irregular mass of camphor in an atmosphere of camphor vapour, there is a constant interchange of state for the molecules at the surfaces of the solid, molecules previously

solid are getting too far off and becoming gas, and molecules previously gas are beating upon the solid and staying there; thus the state of equilibrium is when, as a whole, there are as many molecules which fly off and become gas as fly on and become solid. On a projecting point of the solid the chances are in favour of more flying off than on; in a re-entrant angle the reverse is true. Theoretically, then, the piece ought ultimately to become a sphere, not only by the rounding down of the corners, but by the building up of the flat or re-entrant sides. That the corners do round off all know. If this is all true we only need to bring the two pieces together and consider them as one, and the crack between them as a re-entrant angle, and the union is brought about as above indicated. If in the above the word liquid be substituted for vapour or gas, the explanation will apply to the regelation of ice in water at 0°C .

We may go even further and predict a uniting without actual contact, and this prediction has been experimentally demonstrated in the case of ice and water. A large rough block of ice (about fifteen pounds) was sawed nearly in two, the slit washed out and all the fine pieces removed. In this way it was possible to hold two plane surfaces of ice parallel and near each other (1 to 2 m.m.) without danger of actual contact. Into the outer edge of the saw cut a cotton wick was pressed, thus isolating the space between the faces from the outside and preventing any currents from circulating through the crack. The whole block was then placed in water at zero and inclosed in non-conducting cases and left for twenty-five to thirty hours. This experiment was tried three times, and each time a freezing across the space had taken place. The whole space was not filled, but in numerous places, notably along just inside the wicking and up from the bottom of the cut. No doubt the regelation would have gone further if the experiment could have been continued longer. The melting of the whole block puts an end to each experiment. As these experiments were performed in summer, there is scarcely a possibility that the ice was colder than 0°C .

Inasmuch as there appears to be an increasing inclination to regard solutions and alloys as chemical compounds, it seems justifiable to speak of the action according to the alloy law as chemical. On the other hand, there are some cases which at first appear as chemical action between solids, which upon closer investigation can be explained on a simpler assumption.

For example, Mr. W. Spring (*Zeit. Phys. Chemie*, ii., 1888, p. 536), in a recent paper on this subject, cites three particular cases as being chemical action between solids, the union of copper and sulphur, the reaction between copper and mercuric chloride, and between potassium nitrate and sodium acetate.

The formation of the sulphide of copper and other sulphides was accomplished by Mr. Spring by compression of the elements. But it is not even necessary that the sulphur and copper be in contact. I have made the sulphide at ordinary temperatures with the two an inch apart, and a wad of cotton in the tube between them. It is simply the *vapour* of sulphur which attacks the copper. That sulphur gives off a perceptible vapour at ordinary temperatures, especially *in vacuo*, is a fact anyone can easily demonstrate. The case of the copper and mercuric chloride is precisely the same. The *vapour* of the chloride will go through a whole tube past cotton wads and attack the copper, or colour potassic iodide. Hence we can scarcely assert that these reactions are between *solid* bodies. The reaction between potassium nitrate and sodium acetate is equally unconvincing. Mr. Spring expected an interchange of bases and acids and left the mixture of the dry fine powders four months in a desiccator to give time for the exchange. On removing them from the desiccator a deliquescence was noticeable, and he therefore concludes that the interchange had taken place, since the original salts do not easily deliquesce; but the product of the reaction (potassium acetate) does.

It appears to me thus:—The moment the powders were brought to the air, the water vapour enters the operation and we have potassium nitrate, water vapour, and sodium acetate, and the result of their mutual interaction is a solution of potassium acetate and sodium nitrate. In fact, if the dry powdered salts are stirred together, in a very few moments deliquescence begins, showing that whatever the reaction it goes on at once, and is a matter of moments and not of months. Thus even this experiment in its present form does not convince us that a chemical exchange took place *before* the water vapour entered the reaction.

The question of chemical action between solids is by no means new, but is being constantly extended. I may say I believe chemical action may take place wherever the product or products are liquid or gaseous even though the reagents are solid, with perhaps the added condition that one or both the reagents be soluble in the liquid produced. If this be true, my new method of forming alloys is but a special case of the above general principle.*—*Bulletin of the United States Geological Survey*, No. 64.

A METHOD FOR THE QUANTITATIVE SEPARATION OF BARIUM FROM STRONTIUM BY THE ACTION OF AMYL ALCOHOL ON THE BROMIDES.†

By PHILIP E. BROWNING.

THE existing methods upon which dependence can be made in the separation of barium from strontium are few in number. Dr. R. Fresenius, in discussing them through several numbers of his journal (*Zeit. Anal. Chemie*, xxix., 20, 143, 413), concludes that the only one which gives perfectly reliable results consists of the precipitation of the barium by a double treatment with ammonium chromate in acetic acid solution.

Having demonstrated the possibility of separating both barium and strontium from calcium by the dehydrating and appropriate solvent action of boiling amyl alcohol on the nitrates (*Amer. Jour. Sci.*, xliii., 50, 314), the possibility of a similar method of separation by the use of suitable salts of barium and strontium seemed worthy of investigation and necessary to complete the series as applied to this group.

In looking about for suitable salts upon which to experiment, the behaviour of the chlorides was suggestive. Barium chloride is completely insoluble in amyl alcohol, while the corresponding strontium salt is somewhat soluble. The possibility of finding strontium bromide more readily soluble than the corresponding chloride seemed worthy of attention. The method of preparation followed was the treatment of the precipitated and thoroughly washed carbonates of barium and strontium with hydrobromic acid (*Proc. Amer. Acad.*, xvii., p. 30), prepared by mixing definite proportions of potassium bromide in solutions with sulphuric acid and water while hot, filtering off the potassium sulphate which separates on cooling, and re-distilling the filtrate until the distillate contains no appreciable trace of sulphuric acid. The standards of the solutions of barium and strontium bromides made in this way were determined by precipitating definite portions, measured and weighed, with sulphuric acid,—the strontium, after the accepted method of adding ethyl alcohol to increase the insolubility, and

the barium, after the manner suggested by Dr. F. W. Mar (*Amer. Jour. Sci.*, xli., 288), precipitating with an excess of sulphuric acid in the presence of hydrochloric acid. The mean of closely agreeing results was taken as the standard. Preliminary experiments on the bromides formed in this way gave encouraging results, the barium salt appearing to be almost completely insoluble, while the strontium salt dissolved freely.

The first series of experiments were directed toward a quantitative determination of the solubility of barium bromide in the alcohol. Definite portions of the standardised solution of barium bromide were measured from a burette into counterpoised beakers of about 50 c.m.³ capacity, and weighed as a check on the burette reading. This solution was then evaporated to dryness, and the residue was dissolved in a few drops of water and boiled with 10 c.m.³ of amyl alcohol. The separating bromide was filtered off on an asbestos felt contained in a perforated platinum crucible, the whole having been previously ignited and weighed. The crucible containing the bromide was at first dried at 140° to 150° C. in an air-bath after the manner described in the previous papers, and weighed. The unsuccessful attempt to get a constant weight, however, proved the impossibility of weighing as bromide, the weight decreasing rapidly with each successive drying. It was deemed best accordingly to dissolve the bromide from the felt into a beaker placed to receive it, and to precipitate with sulphuric acid in the presence of hydrochloric acid, after the same manner followed in the determinations of the standards. The precipitated sulphate, which in a few minutes settles completely, was filtered off upon the same felt from which the bromide had been dissolved, dried, ignited to low redness, and weighed.

Series I. gives the results of several experiments made after this manner, which show the solubility of the barium salt to be about 0.0013 grm. on the oxide in 10 c.m.³ of amyl alcohol. The filtrate, after boiling with amyl alcohol, was evaporated, and the residue was treated with sulphuric acid and weighed; or the filtrate was precipitated directly by adding sulphuric acid, enough ethyl alcohol being added to secure thorough mixture. The amount of sulphate found agreed uniformly with the loss determined in the residue after boiling. A portion of the salt, which dissolved in the alcohol on being examined before the spectroscope, gave only the green bands characteristic of barium.

SERIES I.

	BaO taken. Grm.	BaO found. Grm.	Error. Grm.
1.	0.1234	0.1222	0.0012—
2.	0.0824	0.0809	0.0015—
3.	0.0823	0.0809	0.0014—
4.	0.0818	0.0803	0.0015—
5.	0.0733	0.0720	0.0013—

Several methods of treatment were followed to prevent if possible this solubility, such as the addition of a few drops of hydrobromic acid before boiling, of the same after the barium bromide had separated, of a few drops of ethylene dibromide or ethyl bromide at the completion of the boiling, of a few drops of bromine water before boiling, &c. The results of these experiments showed these modifications to be of little or no value.

On boiling the strontium bromide with the alcohol, slight spots separated occasionally, which, on the addition of a drop of hydrobromic acid, went into solution and did not appear on re-boiling. In order to determine the solubility of the strontium bromide in the alcohol, a saturated solution was obtained by boiling an excess of the strontium salt with the alcohol, the salt in a measured portion of 10 c.m.³ was precipitated as sulphate by the addition of ethyl alcohol and sulphuric acid, and weighed. Duplicate determination showed the solubility to be about 0.2 grm. on the oxide in 10 c.m.³ of the alcohol. The mode of procedure for the separation of these elements

* Experiments endeavouring to produce carbon disulphide from the elements at ordinary temperatures are in hand and give promise of positive results. Also, experiments on the interaction of potassium nitrate and sodium acetate have been started; it will, however, be some time before further results can be given.

† From the *American Journal of Science*, vol. xlv., December, 1892.—Contributions from the Kent Chemical Laboratory of Yale college.

was identical with that already described in the case of barium alone, up to the point at which the barium was filtered off, except, of course, the addition at first of a measured and weighed amount of a previously standardised solution of strontium bromide. The strontium was precipitated from the filtrate as sulphate by dilute sulphuric acid, ethyl alcohol being added to secure thorough mixture. These precipitates were generally filtered off upon asbestos felts, and although their gelatinous character delayed the filtration somewhat, the drying and burning of a filter-paper with the possible danger of loss by reduction in the presence of burning paper was avoided.

Series II. gives the results of a single treatment, and it will be seen that there is apparently a slight contamination of the barium by the strontium, which, where the latter is present in large quantities, balances the solubility of the barium (0.0013 grm. on the oxide). Where the amounts of strontium taken are small, the loss of barium due to solubility appears.

SERIES II.

	BaO taken. Grm.	BaO found. Grm.	Error. Grm.	SrO taken. Grm.	SrO found. Grm.	Error. Grm.
1.	0.1228	0.1225	0.0003 -	0.1070	0.1065	0.0005 -
2.	0.1227	0.1231	0.0004 +	0.1074	0.1069	0.0005 -
3.	0.1224	0.1228	0.0004 +	0.1070	0.1067	0.0003 -
4.	0.1217	0.1201	0.0016 -	0.0364	0.0372	0.0008 +
5.	0.1216	0.1222	0.0006 +	0.0133	0.1124	0.0009 -
6.	0.0974	0.0970	0.0004 -	0.0719	0.0721	0.0002 +
7.	0.0971	0.0973	0.0002 +	0.0730	0.0727	0.0003 -
8.	0.0970	0.0971	0.0001 +	0.0718	0.0716	0.0002 -
9.	0.0411	0.0390	0.0021 -	0.0365	0.0385	0.0020 +
10.	0.0243	0.0234	0.0009 -	0.1072	0.1072	0.0000

Series III. gives the result of a double treatment. In this series the contaminating effect of the strontium salt disappears entirely, leaving a deficiency of about 0.0025 grm. on the oxide to be added to the barium, and a corresponding amount of sulphate (0.0040 grm.), to be subtracted from the strontium sulphate before calculating it to the condition of the oxide. The manipulation is the same as that outlined for the single treatment, as far as the completion of the first boiling. At this point the amyl alcohol containing most of the strontium in solution was decanted upon a weighed and ignited felt, and collected in a beaker placed to receive it. The residue of barium, with traces of strontium, was then dissolved in a few drops of water, a drop of hydrobromic acid was added, and the boiling was repeated with another portion of 10 c.m.³ of amyl alcohol. Upon reaching the boiling point of the alcohol the beaker was removed, and the barium salt was filtered upon the felt through which the first portion had been decanted, and treated as before described.

SERIES III.

	BaO taken. Grm.	BaO found. (Correc.) Grm.	Error. Grm.	SrO taken. Grm.	SrO found. (Correc.) Grm.	Error. Grm.
1.	0.1212	0.1219	0.0007 +	0.1068	0.1071	0.0003 +
2.	0.1215	0.1219	0.0004 +	0.0358	0.0359	0.0001 +
3.	0.1220	0.1221	0.0001 +	0.0353	0.0347	0.0006 -
4.	0.1212	0.1220	0.0008 +	0.0363	0.0358	0.0005 -
5.	0.1219	0.1221	0.0002 +	0.0361	0.0354	0.0007 -
6.	0.1211	0.1218	0.0007 +	0.1126	0.1116	0.0010 -
7.	0.1319	0.1319	0.0000	0.0577	0.0586	0.0009 +
8.	0.0496	0.0492	0.0004 -	0.0574	0.0579	0.0005 +

The method is rapid, and while the correction to be applied owing to the solubility of the barium salt is large it is so definite that it cannot be objectionable. The author, in conclusion, would express his indebtedness to Prof. F. A. Gooch, of the Kent Laboratory, for the many helpful suggestions received from him bearing upon this investigation.

ON GLYCERIN.*

By J. LEWKOWITSCH, Ph.D.

At the outset, I wish to disclaim any intention on my part of bringing anything new before you. But having been asked to say something about glycerin—with the manufacture of which I am connected—I thought I might perhaps supplement the remarks made last year by Mr. Siebold and several other gentlemen, in the discussion following Mr. Siebold's paper.

This will be done mostly from the manufacturer's point of view, as manufacturing processes cannot be supposed to be generally known, and it is not at all unlikely that erroneous opinions may be current amongst those not conversant with practical processes used in chemical works.

During the last year it has been repeatedly stated that some samples of glycerin destined for pharmaceutical purposes contained arsenic, a fact which was not unknown to manufacturers, but on which, for very obvious reasons, they did not care to enlighten the consumers. The arsenic in the glycerin owes its existence only to the arsenic contained in the reagents used in the manufacturing process. It has been pointed out by several gentlemen in last year's discussion, that glycerin purified by distillation would not be contaminated by this poisonous substance; although it is but fair to say that Mr. Allen had some doubts about it, still, in the concluding remarks it was distinctly stated that arsenic could be removed by distillation.

This is not so, as the simple fact will show that nowadays all glycerin for pharmaceutical purposes is distilled, nay, even double distilled, glycerin. The times when glycerin was being prepared by other processes of refining have gone by, and a glycerin which had not been purified by steam distillation would be unsaleable for pharmaceutical purposes.

But to remove every doubt, I prepared the substance formed when arsenious acid is dissolved in glycerin, a substance which has been described by Schiff, and later on by Jackson, who apparently overlooked the earlier publication of Schiff. This substance is the arsenious ether of glycerin, $\text{AsO}_3(\text{C}_3\text{H}_5)$. On being heated to 250° C., it decomposes, while arseniuretted hydrogen and other volatile arsenious compounds distil over. At the same temperature glycerin distils also over, and it is quite evident therefore that any arsenic contained in glycerin will distil along with it. The experiments which I carried out could not show any other result.

Arsenic contained in glycerin cannot be removed by distillation, and to my knowledge there is no process known for completely freeing glycerin from arsenic on a practical scale.

Pure glycerin, free from arsenic, can therefore be obtained from such sources only where reagents not contaminated with arsenic are being used. As it has been suggested last year that glycerin emanating from certain processes ought to be rigorously excluded by the Pharmacopœia, I may be allowed here to very briefly review from our point of view the processes used for manufacturing glycerin. The raw materials are exclusively fats and oils which yield on saponification or hydrolysis the glycerin as a by-product.

Glycerin free from arsenic will be obtained in those processes where the fats are hydrolysed by means of water, whether it be used in the liquid state, under high pressure, or as superheated steam. The lime saponification, which is yet largely practised, especially in smaller works, will, as a rule, also yield an arsenic-free glycerin. On the contrary, all glycerin coming from works where the sulphuric acid saponification is practised, will contain arsenic, as the glycerin will extract all the arsenic from the sulphuric acid. There is, however, no doubt that

* British Pharmaceutical Conference, Leeds.

even such glycerin would be pure, as far as arsenic is concerned, if sulphuric acid free from arsenic were used, as it may be prepared from the sulphur obtained by Chance's process.

There is consequently no doubt that there are sources from which one may easily obtain a pure glycerin. With a view to ascertain whether there are in commerce samples of glycerin absolutely free from arsenic—for in many works several processes are simultaneously used, and the glycerin will be mixed in the end—I examined ten samples of glycerin coming from ten different works. As I wished to detect smallest traces, I used silver nitrate instead of mercuric bichloride. Three of the samples would have to be rejected, four samples contained very small traces, which might be disregarded, while three only were absolutely free from arsenic.

There is still another process for saponifying fats, and consequently manufacturing glycerin, practised on a very large scale indeed, that which yields the soap-lye glycerin. At last year's Conference the glycerin derived from that source was very badly treated, and it was demanded that soap-lye glycerin ought to be entirely excluded from pharmacy. Unnecessary precaution!—up to now, at least; for no chemically pure glycerin has been prepared hitherto from soap lees, owing to the difficulties incident to the purification of it.

Being wishful to prove here that soap-lye glycerin has a far worse reputation than it—or, let me say, some of it deserves, I undertook during the last few weeks to prepare chemically pure glycerin from soap-lees, not in the laboratory, but on a large scale, in the works. I had to use such glycerin as I just had at hand, and as this contained, owing to the impure reagents, some arsenic, I had on starting to expect a glycerin containing traces of arsenic; but this is, from reasons pointed out above, only of secondary importance, as on repeating the manufacture of it, I shall have to start with purer reagents, and the real difficulties are lying in quite another direction.

Arsenic, although the most objectionable impurity, is, however, not the only one which may be found in "chemically pure" glycerin. As the British Pharmacopœia treats glycerin somewhat cursorily, I may be allowed to point out here one or two tests which will perhaps be found useful.

The glycerin may contain organic impurities, either fatty acids, &c., or so-called polyglycerols, under which name I may summarise all those substances having a higher boiling point than glycerin itself. The way to test for the latter is to gently evaporate a known quantity of glycerin in a platinum dish at a temperature of 160° C. The residue left, from which the ash, subsequently found on incineration, has to be deducted, will give a fair indication as to the care with which the glycerin has been distilled.

The following table gives the residues for eight "chemically pure" glycerins, arranged according to the quantity of organic residue, to which I have added the analysis of the soap-lye glycerin:—

	Organic residue. Per cent.	Ash. Per cent.
1	0.0243	0.00603
2	0.0327	0.0050
3 (a)	0.0328	0.0140
(b)	0.0267	0.0102
4	0.0360	0.0138
5	0.0371	0.0081
6	0.0443	0.0066
7	0.0738	0.014
8	0.0751	0.0154
9	0.0931	0.0305

No. 3 represents the figures found for two batches of the soap-lye glycerin, which I have shown.

Fatty acids, as butyric acid, &c., and other organic impurities will be easily detected by testing with ammoniacal silver nitrate at ordinary temperature, which is

recommended by the German Pharmacopœia. It is required of a good glycerin that it should not reduce the silver within fifteen minutes. This test is far more delicate than that in which silver nitrate alone is used, as the manufacturers of cosmetics do, who reject any glycerin which reduces silver nitrate in less than twenty-four hours. I think that the test with ammoniacal silver nitrate is a little too rigorous, as ammoniacal silver nitrate is easily reduced by glycerin at an elevated temperature; in fact, of all the glycerin samples I examined, there were only two (Continental ones) which fairly responded to this test, while all others would have to be rejected. Testing with nitrate of silver alone would perhaps be sufficient to show whether there are any silver nitrate-reducing substances in the glycerin.

Under No. 68 of the blue list an answer is requested to the question how to estimate glycerol in pharmaceutical preparations. I am afraid there is no satisfactory answer to that question, as we are not yet in possession of sufficient quantitative material. Lately, two methods have been proposed for the estimation of glycerol, which seem specially suitable in a great many cases, unhappily not in all. The first method, based on oxidation of glycerol to oxalic acid, can only be of use where no other organic substance is present which might yield oxalic acid. The glycerol in glycerinum aluminis might be thus estimated. The second method—boiling of glycerol with acetic anhydride and sodium acetate—requires highly concentrated solutions, and would, of course, be completely useless when other substances are present which combine with acetic anhydride, as would be the case with *e.g.*, glycerinum acidi carbolici, or glycerinum acidi gallici and glycerinum acidi tannici. For such preparations it would be required to have a method for completely transforming the glycerol into a weighable substance, *e.g.*, a tribromine derivative.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, January 13th, 1893.

Prof. G. F. FITZGERALD, M.A., F.R.S., President, in the Chair.

MR. HAZELFOOT was elected a member of the Society.

Mr. F. W. SANDERSON, M.A., read a paper on "Science Teaching."

In this communication the author considers the methods of teaching physical science, and remarks that other sciences may best be treated in some different manner.

The method recommended is one found suitable in public schools where boys may remain till about the age of nineteen. In elementary and secondary schools modification would be necessary with a view to making it more immediately useful, whilst in university and technical colleges other methods might be preferable. The object of his public school method was to make physical science a definite means of education, rather than to produce skilled physicists. Certain mathematical subjects, such as arithmetic, geometry, and algebra, should be taught before physics is begun, and taught in such a way as to aid subsequent physical work.

In teaching arithmetic it is deemed advisable to distinguish between the science and the art of it, and to have separate hours for instruction in each. The subjects included in each part are described in some detail in the paper. No existing arithmetic satisfies the author's requirements.

Geometry is considered of the first importance; practical geometry and the use of instruments forming the best introduction to the subject. It is recommended that the

elementary part be taught by the mathematical master, with a view to formal geometry, *e.g.*, Euclid. As most practical geometries consist of isolated constructions, they are useless for teaching the subject in a scientific manner. A number of problems suitable for a graduated introductory course are given.

After elementary geometry, mensuration may be taken up with advantage, the facts being verified by drawing to scale, measuring, or by weighing, but no rules being given.

Trigonometry of one angle may then be commenced. Here also free use should be made of the drawing-board, each pupil finding the sines, cosines, and tangents of angles by drawing and measurement, and making tables.

Quite independent of the mathematical class, the author has been in the habit of carrying boys on the engineering side through a course of graphical analytical geometry, in which they draw straight lines and the quadratic curves, &c., from their equations, solve simultaneous linear equations, quadratics, cubics, &c. Other geometrical constructions follow.

The subject as to what branches of science should be taught in the different departments of a school is then considered, and schemes are given for the classical, modern and commercial, science, and engineering sides.

Some general principles which have been kept in view in arranging the physical teaching are next described. In the first place, the fundamental experiments and observations on which each scientific law is based are explained to the pupils, and when possible the experiments are performed by the boys in the laboratory. Secondly, from the experiments the laws are stated as precisely as possible, the form of statement depending on the knowledge possessed by the class. The problem of expressing a law mathematically from its most fundamental statement is then fully considered. Thirdly, mathematical deductions from the laws are followed out, and the pupils perform experiments to verify results, and thus confirm the laws. Fourthly, a course of exact physical measurements is given, which includes mensuration, hydrostatics, mechanics, sound, heat, electricity, and light.

A first and second year's course is arranged in each subject, and in both years all the boys work the same experiment at the same time. This necessitates multiplication of apparatus, but being of a simple character in the lower forms, where the pupils are numerous, it is not prohibitive. It is also stated that boys get better results with comparatively rough apparatus, if large, than with delicate and expensive instruments. About half the time devoted to physics is spent in the laboratory.

Mathematics is introduced as far as can be done without straining the pupils too much, and with young classes appeal is made to experiment where the strictly logical argument would be difficult to follow.

Instead of teaching the applications of science as done in some technical schools, the author's method is to teach pure science, and let the applications come in as illustrations.

At the end of the paper detailed lists of experiments for practical courses in electricity and optics are given. Samples of the apparatus used were exhibited at the meeting, those for optics being particularly simple and ingenious.

Prof. A. M. WORTHINGTON said his experience led him to a very hearty agreement with Mr. Sanderson on all essential points, and he thought there was now a close agreement amongst teachers as to the best methods. He therefore wished to ask: Had not the time now come at which the Physical Society might usefully endeavour to exert direct influence on science teaching? As the scientific instruction of a person who intends following a scientific calling is generally divided into stages and conducted in different places under different teachers, he thought it was desirable that those in charge of his training at each stage should say up to what point his instruction should be carried before he reaches them.

Other matters in which the Society might do useful work were, first, reporting on text-books and condemning the bad ones, and, second, furthering the adoption of the decimal system.

At present, he said, an enormous extension in the teaching of physical science is taking place, and it seemed within the power of the Physical Society to place itself at the head of the movement. Another point which required to be settled was the relative importance of physics and chemistry at different stages of a student's education.

Mr. L. CUMMING agreed with the general principles laid down by Mr. Sanderson. In attempting to carry out such schemes numerous difficulties presented themselves, especially where the science master had not control over the subdivision of the boys' time. He had tried teaching the science of arithmetic to boys in the lower forms, but the results were not encouraging, for he found very few who could do much in it. They seemed to devote themselves much more readily to concrete problems and the art of manipulation of rules. Graphical statics was very valuable. As regards experimental lectures, he believed them to be very important, especially in junior classes. For scholarship boys a different method had been tried with success. Instead of performing lengthy experiments completely before the class, the essential parts were gone over, and for the minor points the results obtained in experiments made before or after the lecture were given, so that all the data for reducing the results were to hand. This saved considerable time. He had hoped Mr. Sanderson would say something about the slide rules, and wished to learn his opinions on its use.

Dr. STONEY said he was very much struck with the methods of teaching brought forward by Mr. Sanderson, and remarked that his own work would have been considerably lightened if such a scheme had been developed many years ago. Experimental methods were very valuable, provided the inaccuracies of measurement be kept in view. Plotting curves was also very instructive, and might be made a means of furnishing the fundamental notions in the differential and integral calculus. As to the introduction of chemistry, his experience went to show that this should be done at an early age. Dynamics should also be begun early.

Mr. W. R. CROFT thought that if the Society did make rules to regulate the teaching of physical science, these rules should not be too strict, for the ages and aims of boys might differ widely. At Winchester the science teaching was carried out on the lines recommended by a committee of the Royal Society appointed to consider the subject. (Leaflets showing the scheme adopted were here distributed to members.) The object of the scheme was not merely to make science a means of education, but an integral part of the education of his pupils. He also made a point of keeping the lecture experiments up to date.

Mr. RENTOUL said dynamics should not be taught as a mathematical subject, but experimentally. He thought it of the first importance that boys should learn how to find out facts for themselves, and for this practical work was essential.

Prof. AYRTON remarked that the conditions under which science was taught differed in different places. He himself taught with the object of enabling the persons under instruction to improve the industry. For this purpose he believed the analytical method more suitable than the synthetical one adopted by Mr. Sanderson. It also had the advantage of being more scientific, for it was more natural, being, in fact, that used by children from birth, for they had no other means of learning the nature and properties of their surroundings. In his first year's technical course the work was synthetical, whilst in the third year, the students having analysed existing apparatus, were taught to devise new or improved forms, and hence the work became more synthetical.

Mr. F. J. SMITH said it was important that students be taught to measure by the balance, micrometer, spherometer,

meter, &c., as soon as possible. He also inquired how far Mr. Sanderson's pupils could help themselves in making the apparatus required for the simple experiments.

Dr. GLADSTONE agreed with many points in the paper. Lately he had had to do with schemes for improving the teaching in elementary schools. Children were naturally philosophers, but at present their curiosity was considered objectionable and sternly repressed. Efforts were now being made to alter this state of things. Kindergarten classes in infant schools were a step in the right direction. It was very difficult to introduce analogous methods in the higher standards, but natural science had now obtained a footing. Although the methods of teaching adopted might be those suitable for pure science, care should be taken to put in practical illustrations, for when suitably chosen, they are sources of great interest to children.

Mr. SANDERSON, in reply, said the slide rule was used throughout the course. Mechanics was taught by actual machines, such as pulley blocks, screw jacks, &c. The boys made some apparatus, but to make all would require too much time.

The PRESIDENT, when proposing a vote of thanks to the author of the paper, said that in Ireland the opinion that boys and girls cannot be taught science greatly predominated. They found considerable difficulty in getting any continuation of the kindergarten teaching sanctioned. Possibly drawing might be allowed, but this seemed all they could hope for at present. He wished to emphasise the fact that in such schools the object was education, and practical applications of science were not important except in so far as they created an interest in the subjects. At present scientific teaching was in an experimental stage, and as in other things, progress is made by trial and error. Many different methods were being tried, and it was important to know which were successful and which failures. He thought the Physical Society might be useful in collecting information on the subject by issuing a circular of questions to science teachers, and subsequently drawing up a report on the subject.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 2, January 9, 1893.

The Drainage Waters of Cultivated Land.—P. P. Dehérain.—The drainage of cultivated soils is much less abundant than that of bare soils, and it is the less the longer the ground is occupied. In agriculture the object to be aimed at is to cover the soil with a plant sufficiently luxuriant in its vegetation to evaporate all the rain-fall. The loss of nitrogen compounds is regulated not by the composition of the drainage, but by its abundance. All the nitrogen nitrified in the soil is either assimilated or lost. Thus, when the crop is small the farmer is doubly injured: by the deficiency of the products obtained and by the impoverishment of his land.

The Purification of Arsenical Zinc.—H. Lescoeur.—Zinc intended for toxicological operations may be obtained by a double treatment: an oxidation with nitre and a fusion with zinc chloride. The metal thus prepared is totally free from arsenic, antimony, sulphur, and phosphorus. It contains iron, lead, copper, &c. But the presence of these metals occasions no inconvenience.

Combinations of Quinoleine with the Haloid Salts of Silver.—Raoul Varet.—Quinoleine in excess, acting upon silver chloride, bromide, and iodide, yields compounds containing 1 mol. of base to 1 mol. of salt. These

compounds are more stable than those obtained with pyridine, probably because the vapour tension of pyridine at the ordinary temperature is considerable. The compounds produced by pyridine and quinoleine, tertiary bases, are less stable than those formed by piperidine, a secondary base. Silver chloride, bromide, and iodide do not dissolve in quinoleine, contrary to what takes place in pyridine and piperidine. This fact is probably due to the presence of the benzenic nucleus in quinoleine. Silver cyanide dissolves very easily in quinoleine, forming a compound containing 2 mols. base to 1 mol. of salt. It is of the same type as that produced by piperidine.

Symmetric Propylurea and Dipropylurea.—F. Chancel.—The author prepares the former substance by the action of propylisocyanate upon aqueous monopropanamine. It melts at 104°, and boils at 255°. It is sparingly soluble in cold water; rather more readily in hot water. Its best solvents are alcohol and especially ether. Dipropylsulphurea melts at 68°.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 5.

Determination of Clay and Sand in Soils.—Dr. F. Tschaplowitz.—In the sense of agricultural and horticultural practice, we may regard as clay all those constituents of the soil free from humus and carbonate which are insoluble in dilute hydrochloric acid and in alkali. It appears that elutriations can be effected with the same certainty in a precipitation cylinder as in Schöne's apparatus. Clay may be opened up by prolonged boiling in a Kjeldahl flask. All equally insoluble material free from humus and carbonate, but of higher hydraulic value than from 0.01 to 0.0006 m.m., is to be regarded as sand.

Analysis of the Nitrogenous Constituents present in Commercial Peptones.—A. Stutzer (of Bonn).—This paper will be inserted if possible.

Determination of Phosphoric Acid in Basic Slags.—Dr. A. F. Jolles (of Vienna).—Already inserted.

Method of Determining Thallium by Titration.—K. Sponholz.—This paper will be inserted in full.

Precipitation of Alumina in Presence of Salts of Lithium.—K. and E. Sponholz.—To be inserted in full.

Proportion of Fluorine in Bones and Teeth.—Dr. S. Gabriel.—This memoir will be inserted in full.

Contributions to Kjeldahl's Process for the Determination of Nitrogen.—Carl Arnold and Konrad Wedemeyer.—(See p. 37).

Analysis of Lard.—C. Amthor and Julius Zinc.—The authors recommend the use of the solution as originally prescribed by Von Hübl.

Quantitative Determination of Antimony and the Gooch Crucible.—Th. Paul.—This paper requires the accompanying illustration.

A Continuous Gas-generating Apparatus.—Alex. von Kalcinsky.—This paper also requires the illustration appended.

Spectra of Copper, Silver, and Gold.—H. Kayser and C. Runge.—From the *Annalen Physik Chemie*. No particulars are given.

Position of Absorption-Bands, and the Sensitiveness of Organic Colouring-Matters to Light.—E. Vogel (*Annalen Physik Chemie*).—No details are given.

Action of Sulphuric Acid, Dilute or Concentrated, upon Potassium and Sodium Bromides and upon Hydrobromic Acid.—Frank T. Addyman.—(From the *Jour. Chem. Soc.*).

Action of Dilute Sulphuric Acid upon Zinc.—Frank Pullinger.—(From the *Jour. Chem. Soc.*).

The Use of Platinum Resistance Thermometers.—H. L. Callendar and E. H. Griffiths.—(From the *CHEMICAL NEWS*).

Researches on the Action of Different Metals, Metallic Salts, Acids, and Oxidising Agents upon Caoutchouc.—W. Thomson and F. Lewis.—(From the CHEMICAL NEWS).

Determination of Melting-Points.—Arnold Reissert (*Ber. Deut. Chem. Gesell.*).—The author has submitted the various methods of determining melting-points to a careful examination, and, like Landolt, comes to the conclusion that not only the various methods of determination yield discrepant values, but even determinations effected on one and the same method do not entirely coincide. The values obtained by the application of capillary tubes are generally too high, especially if the temperature is raised too quickly and the point of complete fusion is observed. The apparatus with a ball signal also gives too high results, and the higher the more rapidly the temperature rises. The method recommended by Landolt as the most accurate requires at least 20 grms. of substance, and is therefore in most cases inapplicable, so that the use of capillary tubes must be retained in practice. To obtain the most accurate results possible, the author recommends the following precautions. 1. The zero-point of the thermometer, used for the determinations, must be determined from time to time, and the corresponding correction must be made. 2. The correction for the projecting mercurial filament must always be made, as without it differences of several degrees may be produced in consequence of the different error. The excellent tables worked out by Reinbach greatly simplify the application of this correction. 3. The point of incipient melting should always be taken (in pure substances only!), as the temperature in the interior of the capillary tube is always rather higher than at the sides. An apparatus with an electric signal-bell has been designed by A. C. Christomanos.

Acceleration of Evaporation in Small Vessels.—E. Whitfield.—(From the *Journal of Analytical and Applied Chemistry*).

New Nitrometer for Determining Nitrogen in the Salts of Ammonium.—W. Hentschel (*Berichte Deut. Chem. Gesell.*).—A description of this apparatus is of little use unless illustrated. According to the inventor, no corrections are necessary except the utmost accuracy is required, since the absorption of the nitrogen in the hot liquid is essentially less than in such of ordinary temperature.

MEETINGS FOR THE WEEK.

- MONDAY, 30th.—Medical, 8.30.
— Society of Arts, 8. "The Practical Measurement of Alternating Electrical Currents," by Prof. J. A. Fleming, F.R.S. (Cantor Lectures).
- TUESDAY, 31st.—Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
- WEDNESDAY, Feb. 1st.—Society of Arts, 8. "The Purification of the Air Supply to Public Buildings and Dwellings," by William Key.
- THURSDAY, 2nd.—Royal, 4.30.
— Royal Society Club, 6.30.
— Chemical Society, 8. "The Connection between the Atomic Weight of the Contained Metals and the Magnitude of the Angles of Crystals of Isomorphous Series," by A. E. Tutton. "Note on Optical Properties other than Colour as indicative of Structure," by Prof. H. E. Armstrong. "Contribution to the Knowledge of the Aconite Alkaloids. IV. Napelline," by Prof. W. R. Dunstan and E. T. Harrison.
— Royal Institution, 3. "Tennyson," by the Rev. Canon Ainger, M.A., LL.D.
- FRIDAY, 3rd.—Royal Institution, 9. "Theory and Practice in Electrical Science," by Alexander Siemens, M.Inst.C.E.
— Geologists' Association, 7.30. (Anniversary).
— Quekett Club, 8.
— Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.
- SATURDAY, 4th.—Royal Institution, 3. "Expression and Design in Music," by Prof. C. Hubert H. Parry, M.A.

TO CORRESPONDENTS.

E. Woodhead.—No method is known by which the yellow modification of iodide of mercury can be rendered permanent so as not to change easily into the red iodide.

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1732.

FEB 9

KOENE AND STAS:

CHEMISTRY AT BRUSSELS IN 1840—1860.

By Dr. T. L. PHIPSON, F.C.S.;

Formerly of the University of Brussels; Member of the
Chemical Society of Paris, &c.

SHORTLY after the Revolution of September, 1830, which resulted in the division of the Netherlands into two independent kingdoms, the people of Brussels deemed it necessary to found a University. So, one fine day, a number of good citizens, headed by the Burgomaster, proceeded to the Hotel de Ville, and, after listening to a magnificent piece of music performed by the orchestra of the Royal Harmonic Society, delivered some enthusiastic speeches, and the University of Brussels was duly called into existence with all proper forms and ceremonies (Oct. 20, 1834).

Fifteen years later, I became enrolled as a student in that University, where I passed some of the happiest years of my life. After a long course of Philosophy, I entered the faculties of Science and Medicine, devoting particular attention to chemistry under Prof. C. J. Koene, the rival of Stas. The latter was Professor of Chemistry at the Ecole Militaire, and Melsens, another well-known chemist, lectured at the Ecole Vétérinaire.

Koene was a disciple of Berzelius, he was a Doctor of Science, and had gained his professorship by dint of hard work and indomitable application; he enjoyed no patronage whatever. Berzelius himself had translated into Swedish Koene's paper on "Aqua Regia," and inserted it in the *Transactions* of the Academy of Stockholm.

Stas, like the worthy chemist Melsens, was highly recommended as the pupil and friend of Jean Baptiste Dumas, with whom they had both worked in Paris, and to whose powerful patronage Stas owed everything. I am not aware that he ever graduated in any University, but after having obtained the Professorship of Chemistry at the Ecole Militaire, he succeeded in getting himself elected into the Belgian Academy of Sciences, and, many years later, as a Corresponding Member of the Paris Academy. As an old pupil and *collaborateur* of Dumas, he, of course, brought forward the new theories of the latter, which were combatted by Berzelius and by Koene, but he had no great field for developing them; young soldiers, as a rule, make poor chemists.

At the University, where the doctrines of Berzelius, Mulder, and Liebig were professed in the most able manner by Dr. Koene, the new ideas in organic chemistry then cropping up were rather rather severely criticised, if not ridiculed, and it was plainly predicted that should they gain ground, they would lead organic chemistry into a state of chaos. Some of my friends are inclined to think that this prediction has been tolerably well realised.

What first brought Stas into notice in Brussels was the celebrated "Affaire Bocarmé," in which a certain Count Bocarmé had poisoned his brother-in-law by means of nicotine, which he obtained by distilling tobacco leaf. In these operations, it was said, his victim occasionally assisted him. Koene was (or pretended to be) much hurt that the Government called upon Stas, who was only Professor of the Ecole Militaire, to make the chemical investigations in this case, which should have been given to the Professor at the University. Stas found nicotine in the body, but only—as Dr. Koene took care to remind his pupils—after he had found two bottles of it in a cupboard. Anyhow, this affair led Stas, after the execution

of Count Bocarmé, to the publication of an important paper on the isolation of alkaloids in cases of poisoning, which has proved of considerable value to science.

Koene was a very expert chemist and an excellent professor.* In his lectures he rarely referred to notes. There were a few specimens and flasks on the table before him, and a large black board behind him, to which he turned now and then and covered it with formulæ. To his left stood the docile laboratory assistant, a dull timid individual, who once allowed the air to get into a large jar of phosphuretted hydrogen as he carried it from the laboratory to the adjacent lecture room, making his entry with a flame which rose to the ceiling; and on the right of the professor was a large Dutch stove, which in winter proved a great comfort, as the lectures began at eight in the morning.

He had also a course of toxicology in the afternoon at three o'clock, twice a week. Besides his professorship at the University, Koene held the appointment of superintendent or consulting chemist to the Mint, and to the large chemical works of Van der Elst,† and was occasionally engaged on Government Commissions. On such occasions he was frequently thwarted by Stas; for between these two professors there existed very great jealousy. It was an open secret that Stas envied Koene his chair of chemistry at the University; whilst Koene was no less vexed at seeing Stas elected a member of the Belgian Academy of Sciences, and used to speak of him sarcastically as "*the savant*," &c. Although a man of kindly disposition, and a warm-hearted friend, Koene's excessive pride and violent temper, no less than his comparatively short life, strongly militated against his successful competition with a cool-headed man of the world like Stas, who has outlived him by about thirty years. Nevertheless, the "*Mémoires de Chimie*" which Koene has left in one small volume form a lasting monument of ingenious, indefatigable study, and may have their influence on the progress of chemical thought when some of our modern theories are abandoned. He has, among other things, the merit of having reformed our ideas of *neutrality*, and his views were soon universally adopted.

When we compare the work of Koene with that of Stas, it is easy to see that the former possessed the more expansive mind. While Stas limited himself to a small point of philosophy, and to a few purely analytical problems, Koene in his lectures and writings covered a much larger field of thought. We may admire Stas as a laborious painstaking specialist, not without a certain amount of genius; but Koene was possessed of far greater originality of views, and of an impetuous character, which, combined with an ardent love of truth, caused him to grapple with many of the greater phenomena of Nature.

Koene was the first who made use in his lectures of the pure nomenclature of Berzelius; whilst the French professors and their followers used such terms, for instance, as "sulphate of protoxide of iron," "sulphate of peroxide of iron," Koene invariably said "ferrous sulphate," "ferric sulphate," and so on, throughout the whole of inorganic and organic chemistry, just as we have lately begun to do in England. In organic chemistry the *compound radical* theory was used with rare talent. The *equivalent notation* and *dualistic system* (devoid of all hypothesis) were alone used, and in the entire course of the lectures nothing was stated that could not be verified by actual experiment. For instance, MO, HO was not allowed to be MO_2H , since HO could be separated by the mere action of a slight heat, and the supposed body MO_2 could not be isolated, whilst MO could be, and was known to exist, &c.

* He was a powerfully built man, of medium height; black hair, eyes, and beard; and swarthy complexion; with a Roman nose, and decided Jewish aspect; always extremely plain and neat in his attire; he usually wore black silk gloves when walking. His manners were polished and modest, unless when irritated, then his dark gypsy-like eyes would flash fire, and his amiable qualities disappeared.

† Pierre Van der Elst, the founder of these works, was the first to erect leaden chambers for sulphuric acid—this was in the year 1763.

In 1856 was published the first part of Koene's "Mémoires de Chimie" ("Mémoires de Chimie," par le Dr. C. J. Koene, Professeur de Chimie et de Toxicologie à l'Université de Bruxelles. Première Partie. Bruxelles: P. Larcier, Libraire de l'Université, 1856). This little volume comprises papers reprinted from the *Bulletin de l'Académie des Sciences*, of Brussels, *Poggendorff's Annalen*, and the *Annales of the Academy of Sciences* of Stockholm. Others which have appeared in the *Annales de Chimie et de Physique*, and in certain periodicals devoted to agriculture, were, unfortunately, never collected. At the same time, he published a volume of "Popular Lectures," consisting of four public lectures delivered in the Academical Hall of the University and reproduced by A. Tardieu, stenographer to the Legislative Assembly. It is there he discusses the probable constitution of the atmosphere from remote geological ages to the present time, criticising the views of Berzelius, Mulder, Dumas, and Liebig on this interesting subject; and there is also a very severe criticism of a report by Stas on the acid emanations from the chimneys of the Mint, which, I remember, caused great laughter among the crowded audience.

Koene's paper on the neutrality of salts, published in 1842, is a marvel of chemical reasoning, and had great effect on the science of his day; and the same may perhaps be said of his paper on "Aqua Regia," his "Lessons on the Constitution of Salts," and several others.

Stas had, no doubt, enjoyed a far better laboratory training than Koene. Clever and painstaking analyst as the latter may have been for that period, he had not had the advantage of working with Dumas in Paris, and the Belgian Government knew what it was about in confiding to Stas, instead of to Koene, the toxicological investigations in the Bocarmé case. With regard to the extreme care taken by Stas in his investigations on *acetal*, on the *amniotic fluid* of the fowl, and on the *atomic weights* of certain elements with the view of deciding for or against the law of Prout, &c., no doubt the greatest accuracy that could be obtained in the laboratory is made manifest. Nevertheless, Prof. Hinrichs has lately shown (*Comptes Rendus*, Dec., 1892) that the oxygen figure in Stas's determinations with potassic chlorate, increases with the quantity of salt taken for analysis by the dry method, and decreases with the quantity taken when the wet method is used; reminding us, once more, that perfection is not attainable in this world.

It will be gleaned from these considerations that at Brussels, during the period of which I write, we had in Koene the last representative of the great schools of Berzelius and Liebig; and in the persons of Stas and Melsens the first representatives of the new French school. They were all highly meritorious chemists, but Melsens was perhaps the greater philosopher of the three, a man of an exceedingly amiable disposition, and universally beloved by his friends and pupils. Had Stas been at the University instead of the Ecole Militaire he might have drawn around him young men devoted to science. Koene's classes, like those at Edinburgh at the present day, were filled almost entirely by medical students. The University in Brussels made few scientists, philosophers, or diplomatists. It was the resort of men destined to live by law or by medicine, and it was a matter of surprise and some talk in the Brussel's newspapers when my paper on "Catalytic Force" took the gold medal in the public competition of the Société Hollandaise des Sciences at Haarlem (1857). Koene was more proud of this than if he had written the paper himself, and took care to remark that no pupil of Stas had ever done such a thing.

Poor Koene was dead when another gold medal fell to my lot in 1868 from the Royal Society of Medical and Natural Sciences of Brussels. His successor, Jean Baptiste Francqui, obtained his doctor's degree six months later than I did; he was elected professor when I had already left Brussels for Paris. Francqui was one of

Koene's favourite pupils and a scientific chemist of great promise, who, after visiting, at the request of the Belgian Government, the principal laboratories in Europe, superintended the re-construction of those at the University of Brussels. He unfortunately succumbed to illness very early in life. Most of Koene's other pupils were destined for pharmacy or medicine, and some of them have become very distinguished men in their respective professions. The pupils of Jean Servais Stas were drafted into the army on leaving the Ecole Militaire. As I have already stated, Stas has outlived Koene by about thirty years, during which time his reputation as a careful analyst and scientific chemist has become greater than it was at the time of the Bocarmé affair, which first brought him into notice.

I hope some day to examine Koene's theory of the constitution of the atmosphere, for which I have no space here. The foregoing remarks will, I trust, prove interesting at a time when the career of Stas is attracting so much attention at the Chemical Society.

Putney, Jan. 27, 1893.

ON POISONING BY TINNED BEEF.

By THOMAS K. LEWIS.

TWENTY cases of poisoning resulted from eating canned corn beef, sold October, 1892. The symptoms of poisoning were noticed in from two to five hours after eating.

Eighteen hours after the meat was sold a preliminary examination was made for lead and tin. The physicians attending the persons stated that they thought that the poisoning was due to inorganic poisons coming from the action of the meat on the can.

About 50 grms. of the meat was burned to a light ash, and tested for tin and lead. Nothing but a small quantity of iron in harmless quantities was found, and which is found in all meat.

Ptomaines were suspected, and then a systematic examination was made for them.

An alcoholic extract was made. The meat was minced finely and well shaken with an equal weight of absolute alcohol for some time, the meat and alcohol being heated to 75° C. The alcohol was filtered away and evaporated by means of a water-bath and air-pumps. The bath was not allowed to reach a temperature higher than 75° C. The solution by this means only reached 40°—45° C. Evaporation continued until a thick extract remained containing some fat, which was dissolved by the alcohol in the extraction from the meat. This fat, which was now precipitated, was filtered away from the extract, which was diluted with a small quantity of absolute alcohol, and evaporated again. A reddish yellow liquid resulted, which had a very sickening odour.

Tests were made as follows:—From an ethereal extract potassium ferricyanide and ferric chloride were mixed, and a few drops of the extract added, which produced a deep blue colour in a few minutes. This showed a reduction of the ferri- to the ferro-cyanide of iron, which is the most satisfactory test we have for ptomaines.

Another test:—A solution 1 to 10 of ether was made of the extract, and a few drops of strong H₂SO₄ was added. A yellow and then a rose-red colour was noticed, also a very prominent odour of amines.

After eighteen days the same methods were employed without success, for no tests could be obtained.

When the meat was first analysed it was used to experiment on animals. It was found to be poisonous to them. Eighteen days after the poison was discovered the meat was again fed to some animals; no symptoms of poisoning occurred.

From the foregoing data, after having consulted "Blythe on Poisons" and "Prescott's Organic Analysis," and several minor works, the following was decided:—

That there were no inorganic poisons, lead or tin, present in the meat, because they were not found by testing, and because no poison was found in the meat at the close of the work.

The poison must have been decomposed, a thing which could not have occurred had it been inorganic poisoning. Hence ptomaines were indicated both by tests and by the poison having decomposed.

Further, a ptomaine called neuridine has been recorded, which decomposes a short time after it has been formed. Therefore we would state that the poison was a ptomaine, and would identify it as neuridine.

Ohio State University, Columbus, Ohio,
January 9, 1893.

A NOTE ON THE
METHOD FOR THE QUANTITATIVE
SEPARATION OF STRONTIUM FROM CALCIUM
BY THE ACTION OF
AMYL ALCOHOL ON THE NITRATES.*

By PHILIP E. BROWNING.

RECENT work on my method for the quantitative separation of strontium from calcium by the action of amyl alcohol on the nitrates (*American Journal of Science*, vol. xlv., December, 1892) has demonstrated the possibility of using very much smaller amounts of amyl alcohol in the boiling than the amounts formerly used (30 c.m.³ for each treatment). By the use of smaller beakers (50 c.m.³ capacity), 10 c.m.³ of the alcohol can be conveniently substituted for 30 c.m.³, and the correction for solubility of the strontium nitrate is thus reduced from 0.001 grm. on the oxide to 0.0003 grm. in each treatment, and the corresponding amount of sulphate to be abstracted from the calcium sulphate before calculating to the condition of oxide is reduced from 0.0017 grm. to 0.0005 grm. in each treatment. The necessity of a double treatment, or the use of two portions of 10 c.m.³ each of the alcohol, brings the total correction to 0.0006 grm. on the strontium oxide, and 0.0010 on the calcium as sulphate. For ordinary work such a correction may be disregarded. The following Tables give the corrected and uncorrected results.

TABLE I. (Correction Disregarded).

SrO taken.	SrO found.	Error.	CaO taken.	CaO found.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1. 0.0570	0.0565	0.0005—	0.0534	0.0540	0.0006+
2. 0.0573	0.0567	0.0006—	0.0534	0.0543	0.0009+
3. 0.0285	0.0274	0.0011—	0.0272	0.0276	0.0004+
4. 0.0568	0.0560	0.0008—	0.0535	0.0537	0.0002+
5. 0.0568	0.0561	0.0007—	0.0533	0.0535	0.0002+
6. 0.0288	0.0280	0.0008—	0.0271	0.0272	0.0001+
7. 0.1420	0.1416	0.0004—	0.0535	0.0544	0.0009+
8. 0.1419	0.1416	0.0003—	0.0665	0.0669	0.0004+
9. 0.1135	0.1132	0.0003—	0.1066	0.1070	0.0004+
10. 0.1137	0.1126	0.0011—	0.1064	0.1070	0.0006+

TABLE II. (Correction Applied).

SrO taken.	SrO found. (Correc.)	Error.	CaO taken.	CaO found. (Correc.)	Error.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1. 0.0570	0.0571	0.0001+	0.0534	0.0536	0.0002+
2. 0.0573	0.0573	0.0000	0.0534	0.0539	0.0005+
3. 0.0285	0.0280	0.0005—	0.0272	0.0272	0.0000
4. 0.0568	0.0566	0.0002—	0.0535	0.0533	0.0002—
5. 0.0568	0.0567	0.0001—	0.0533	0.0531	0.0002—
6. 0.0288	0.0286	0.0002—	0.0271	0.0268	0.0003—
7. 0.1420	0.1422	0.0002+	0.0535	0.0540	0.0005+
8. 0.1419	0.1422	0.0003+	0.0665	0.0665	0.0000
9. 0.1135	0.1138	0.0003+	0.1066	0.1066	0.0000
10. 0.1137	0.1132	0.0005—	0.1064	0.1066	0.0002+

* From the *American Journal of Science*, vol. xlv., December, 1892.—Contributions from the Kent Chemical Laboratory of Yale College.

A PLATINIFEROUS NICKEL ORE FROM CANADA.

By F. W. CLARKE and CHARLES CATLETT.

DURING the autumn of 1888 we received, through two different channels, samples of nickel ores taken from the mines of the Canadian Copper Company, at Sudbury, Ontario. From one source we obtained two masses of sulphides, to be examined for nickel and copper; from the other source came similar sulphides, together with a series of soil and gravel-like material, seven samples in all. In the latter case an examination for platinum was requested, and in five of the samples it was found, the gravel above mentioned yielding 74.85 ounces of metals of the platinum group to the ton of 2000 pounds. At the outset of the investigation we were decidedly incredulous as to the existence of platinum in such ores; but the discovery of sperrylite by Mr. Wells in material from the same mines gave our work a wholesome stimulus, and the assays were carefully carried through.

The sulphide ores submitted to us from Sudbury were all of similar character. They consisted of mixed masses, in which a grey readily tarnishing substance was predominant, with some chalcopyrite, possibly some pyrite, and a very little quartz. Two samples were examined in mass; one gave 31.41 per cent of nickel with a little copper, the other gave 35.39 per cent of nickel and 5.20 of copper. The nickel mineral itself proved to be a sulphide of nickel and iron, and as ores of that composition are not common, it was thought desirable to examine the substance further.

As above stated, the nickel mineral is the predominating constituent of the masses submitted for examination. It is steel grey, massive, and exceedingly alterable in the air, and its specific gravity, determined by pycnometer, is 4.541. An analysis of carefully selected material gave the following results:—

Ni	41.96
Fe	15.57
SiO ₂	1.02
Cu	0.62
S	40.80

99.97

Neither cobalt nor arsenic could be detected.

The foregoing figures work out sharply into the ratio R : S :: 4 : 5; and approximately into the formula Ni₃FeS₅. If we deduct silica, together with the copper reckoned as admixed chalcopyrite, and re-calculate the remainder of the analysis to 100 per cent, we have the following figures:—

	As found.	Calc. as Ni ₃ FeS ₅ .
Ni	43.18	44.6
Fe	15.47	14.4
S	41.35	41.0
	100.00	100.0

In short, the mineral has the composition Ni₄S₅, with about one-fourth of the nickel replaced by iron. The only known species with which this agrees is Laspeyres's polydymite, of which the Sudbury mineral is evidently a ferriferous variety. What relations it may bear toward beyrichite, pyrrhotite, &c., is as yet a matter of considerable uncertainty. Probably in most cases the nickeliferous constituent of pyrrhotite is millerite, but other sulphides, like the polydymite, may perhaps occur also.

The polydymite which was selected for the above analysis came from the mass in which, in average, 35.39 Ni and 5.20 Cu had previously been found. The mass weighed several kilograms, and was remarkably free from quartz. The same mass, with two smaller pieces resembling it, were also examined for platinum, by the following

method:—One assay ton of the finely ground ore was treated with nitric acid until all or practically all of the sulphides had been dissolved. The dried residue was then assayed in the usual manner; except that, to facilitate cupellation, a little pure silver was introduced into the lead button. From the final bead the silver was dissolved out by sulphuric acid, leaving the platinum in a finely divided grey powder. The latter dissolved easily in aqua regia, and gave all the reactions needful to identify it thoroughly. The results were as follows, "A" representing the large mass in which the polydymite was determined:—

	Per cent.
A, 2.55 ounces Pt to the ton, or	0.0087
B, 1.8 ounces Pt to the ton, or	0.0060
C, 7 ounces Pt to the ton, or	0.0240

That the metal weighed was nearly all platinum is certain; but it may have contained small amounts of other metals of the same group. The material separated was not sufficient to warrant a search for the rarer associates of platinum. Probably the platinum exists in the ore as sperrylite, although this point was not proved. The amount of platinum in the mass most thoroughly examined would require, to form sperrylite, only about 0.007 per cent of arsenic, which is too small a quantity for detection by ordinary analysis. That platinum should exist in appreciable quantities in an ore of such character is something quite extraordinary. Whether it could be profitably extracted is an open question.—*Bulletin of the United States Geological Survey*, No. 64.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1892.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, January 10th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 173 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The condition of the water supply to the Metropolis during the month of December continued to be substantially the same as that prevailing during November, and commented on in our previous report. The proportion of organic matter present, as estimated alike by the oxygen and combustion processes, and by the degree of colour-tint of the water, was not excessive for the season of the year, and just a trifle lower than that present in the previous month's supply. In the case of the Thames-derived water, for instance, the mean proportion of organic carbon amounted to 0.192 part in 100,000 parts of the water, as

against a mean of 0.202 part per 100,000 parts of water in the November supply, the maximum proportion found in any single example examined, or 0.286 part in 100,000 parts, being identical with the maximum met with in the November supply.

With two exceptions only, one recorded as "slightly turbid" and the other as "clear but dull," the whole of the 173 samples examined during the month were found to be clear, bright, and well filtered. In several instances no samples could be obtained from the standpipes during the last week of the month, by reason of the sharp frost then prevailing.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.

ON THE GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

Preface.

FROM his famous research on the composition of water (*Ann. Chim. Phys.*, Series 3, vol. viii., p. 189 *et seq.*) Dumas concluded that, in accordance with Prout's law, the "equivalent" of hydrogen, meaning the ratio $H_2 : O$, is equal to one-eighth exactly, although the exact mean of his nineteen syntheses stood at 0.12515 (corresponding to $H = 1.00120$ for $O = 16$, or to $O = 1598$ for $H = 1$). Feeling convinced that his result was liable to a small negative correction, although he had already allowed for the adventitious water formed from the oxygen of the air which had been present in the dilute sulphuric acid which he used for the evolution of his hydrogen, and seeing that his individual results oscillated between 0.1247 and 0.1256, he had no hesitation in rounding off his mean and adopting 0.12500 as the nett result of his work. Strictly speaking, he had perhaps no right to make even this slight arbitrary correction, but his choice was confirmed very shortly after the publication of his memoir by an independent research of Erdmann and Marchand,† which, if it proves anything, shows that Dumas's adopted value is probably nearer the truth than his uncorrected mean.

With these two investigations before them, all chemists agreed in admitting that, however it may stand with Prout's law, the ratio $O : H$ happens to be equal to sixteen exactly, and they continued doing so until Stas, in the course of his great research, came to determine the silver value of sal-ammoniac; and finding that the weight of sal-ammoniac, equivalent to $Ag = 107.93$, that is to say his " NH_4Cl ," exceeded his sum $N + Cl$ by more than four units, gave it as his conviction that the true ratio, $O : H$, cannot be greater than 15.96, corresponding to $H = 1.0024$ for $O = 16$. But Stas's own result is $H = 1.0075$, and this number, if it has any right to vote, is as incompatible with 1.0024 as it is with 1.0000. But Stas's guess was confirmed subsequently by Clarke, and, after him, again by Lothar Meyer and Seubert, who, in their respective recalculations of atomic weights, both arrived at precisely the same value. It is probably owing to this circumstance that the number 15.96 has been so generally adopted by chemists, and found its way into all the handbooks. All chemists, of course, have not adopted it in the same sense. With many, no doubt, it is no more than the arithmetically correct registration of what they take to be the most probable value for a strictly speaking unknown constant, which, for anything they can know, may perhaps lie closer to, say, 16.05 than to 15.96; but

* *Proceedings of the Philosophical Society of Glasgow.*

† *Journ. Prakt. Chemie*, vol. xxvi., p. 461 *et seq.* Abstract in *Ann. Chim. Phys.*, immediately after Dumas's memoir.

not a few attach to it a higher significance, inasmuch as they take 15.96 to be the true value, and contrast it with the old 16 as with a mere approximation, just as one might contrast Berzelius and Dulong's value, 0.764 for C:O, with Dumas and Stas's 0.7500. Prominent amongst these chemists are Lothar Meyer and Seubert, who, in a memoir published by them in the *Ber. Deut. Chem. Gesell.* in March, 1889, give expression to their conviction in the most emphatic manner possible by insisting that we must henceforth refer our atomic weights not to $O=16$, but to $O=15.96$, for "dieser Wert ist der am meisten verbürgte und deshalb allen übrigen für diese Grösse Betracht kommenden vorzuziehen." But where are the guarantees? A glance at Lothar Meyer and Seubert's book* affords an answer, inasmuch as it clearly shows that their conviction of the correctness of their number is based chiefly upon Dumas's and upon Erdmann and Marchand's quantitative synthesis of water, which both, in their hands, led to the identical value, 15.96 for O:H. But, unfortunately, their calculations rest on a false basis. Their mode of calculating Dumas's determinations is that, viewing his nineteen syntheses as *quasi* one synthesis, they deduce the value O:H from a combination of the sum of Dumas's nineteen oxygen weights with the sum of his nineteen uncorrected water weights, which comes to pretty much the same thing as if they had calculated the constant from the mean of Dumas's "equivalents bruts," meaning the equivalents as they come out, if we neglect the adventitious water produced by the dissolved oxygen in the sulphuric acid used for making the hydrogen. But Dumas, as we see from his memoir, effected the corresponding correction in each of the nineteen cases; and, if we believe in Dumas's work at all, what right have we to discard his corrections on his own numbers? Clearly, none whatever; we must go by his "equivalents corrigés," and their mean is 0.12515, corresponding to O:H=15.98.

To pass to Erdmann and Marchand; they, as Lothar Meyer and Seubert inform us, made eight syntheses, which, if calculated as one synthesis, lead to the value 15.96. But, when we look at the original memoir, we find that E. and M. made two distinct sets of four experiments each. In the first set they weighed their oxide of copper and metallic copper in the ordinary way, and allowed for the displaced air by calculation; in the second they adopted Dumas's plan, and weighed both the oxide and the metal derived therefrom in the same evacuated tube. And in each of these four latter experiments (as also in one of the first series) they took care to free their hydrogen from every trace of atmospheric oxygen by making it pass through a red-hot tube full of metallic copper, and from it through a U-tube charged with fused caustic potash before it reached its destination. In other words, while Dumas corrects for his adventitious water by calculation, they avoid its formation. Their general mean for the weight of water containing one part of oxygen, that is to say, for $H_2O:O$, is 1.12520. But, obviously, their second series is far more reliable than their first, and its mean stands at 1.12492, corresponding to O:H=16.010. And these four determinations, being obtained by a decided improvement upon Dumas's method, are worth as much as Dumas's nineteen; hence the nett result of the two investigations taken conjointly is—

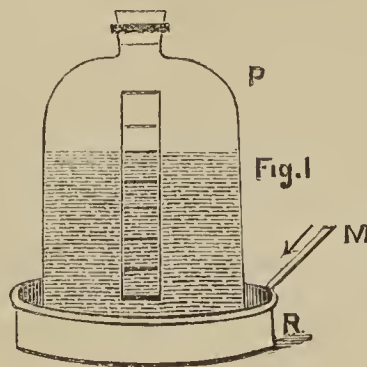
$$O:H = \frac{1}{2} (15.981 + 16.010) = 15.996,$$

or, practically, the exact number, 16.000.

But, supposing even we had nothing but Dumas's uncorrected equivalent to go by, seeing that the nineteen individual values for O:H, as calculated from these, vary from 15.89 to 16.02, it surely is worse than pedantry to swear to that 15.96 as if it were a revelation from heaven! So I thought, some months ago, when, on the basis of little more than a second-hand knowledge of the two researches, I came to speculate on the matter; and, being moreover imbued with a strong mental bias in

favour of Prout's law, I decided upon undertaking an experimental inquiry into Dumas's method-errors, feeling sure in my own mind that I should be able to prove that the old integer 16 is at least as good an approximation to the truth as the fashionable 15.96.

As a first step, I directed Mr. Henderson to set up as close an imitation as possible of Dumas's apparatus for the production of pure hydrogen, and then to determine the oxygen in what we soon came to call "Dumas hydrogen," by filtering a sufficient known volume of the gas through red-hot copper gauze, and weighing the water produced. The result more than confirmed my anticipation, but, while Henderson experimented, I studied Dumas's and Erdmann and Marchand's original memoirs and made an unexpected discovery.



From Dumas's account it appears that, while he weighed his oxide of copper and oxide *in vacuo*, he weighed his water in the air, and that, consequently, his water-weights were liable to be reduced to the vacuum. That a man like Dumas should be capable of omitting this obviously very relevant correction would appear to be an absurd presumption, but the way in which he states his results (on page 200 of his memoir) tends to confirm it. On the table referred to he gives, in so many successive columns, (1) the weight of the water-receptacle before, (2) after the experiment, (3) the exact difference of the two weights as "the weight of water produced," (4) the value $H_2:O$ as calculated from the recorded weights of water and oxygen, and (5) the same corrected for the oxygen introduced as dissolved air with the dilute acid used for the evolution of the hydrogen, as the "equivalent corrigé." Now, if Dumas puts us in a position to check his subtractions, then, assuming that the weighings (1) and (2) as they stand are already reduced to the vacuum, he is surely bound to tell us how he calculated the respective corrections. But he does nothing of the kind. Assuming, as I did at the time, that he simply forgot the vacuum correction, all we can do now is to add to his mean equivalent of hydrogen the weight of air, displaced by 1.12515 parts of water. Assuming, as we may without fear of committing a serious error, that the mean density of the air in which he operated was the same as that corresponding to 15° C. and 760 m.m. pressure, we arrive at the value 0.00138, which raises the equivalent of hydrogen to 0.12653, corresponding to O:H=15.81! But, admitting this to be the real result of Dumas's determinations, how is it that Erdmann and Marchand, who *did* reduce their water-weights to the vacuum (there is no doubt about this, because they give us in each case both the uncorrected and the corrected number), arrived at the value 16.01?

In going carefully over their report, I, at last, come to see my way towards a plausible explanation. As appears from their memoir, they dried their hydrogen finally by passing it through a U-tube, 3 feet long, charged with caustic potash, which, they assure us, dehydrated even a quick current of the gas completely; "because a U-tube filled with fused chloride of calcium, if appended to the outlet end of the potash tube, suffered no change of weight." Their water receptacle was combined with two chloride of calcium tubes to retain the moisture of the

* "Die Atomgewichte der Elemente, aus den Originalzahlen neu berechnet, von L. M. and S." 1883.

surplus hydrogen and of the air which was sent through the apparatus at the end of an experiment. They obviously considered it necessary to prove that fused caustic potash dries a gas completely, but they had no doubt about the efficiency of fused chloride of calcium: and this is no more than was at the time admitted by every chemist. But Fresenius (see his *Zeitschrift* for 1865, p. 177) has since shown that a moist gas, after having been dried exhaustively by even fused chloride of calcium, gives up a quantity of water to oil of vitriol, which, in his trials, amounted to about 1 m.grm. per litre of gas. Now, Erdmann and Marchand's test experiment with their potash tube is quite compatible with the assumption that this tube retained every trace of moisture from the hydrogen which streamed through it, and it is not unfair to assume that the chloride of calcium which Erdmann and Marchand used in their actual *syntheses* was about at a par with Fresenius's preparation. If I am right so far, it follows that Erdmann and Marchand lost about 1 m.grm. of water for every litre of permanent gas which passed through their water receptacle at the end of the experiment; and this, as a little reflection shows, is amply sufficient to account for all the difference between their value for $H_2O : O$ and Dumas's as corrected by me. But this, as I could not help seeing, would only prove that Erdmann and Marchand's determinations must be given up as hopelessly wrong, and, in any case, it still devolved upon me to prove the correctness of my suspicion concerning Dumas's calculations. Obviously, what I had to do was to inquire critically into both Erdmann and Marchand's and Dumas's methods, and besides to carry out at least a few *syntheses* of water according to Dumas's method, to enable myself to decide between his own and my mode of interpreting his numbers. And these "few test *syntheses*" were sure to develop into an independent re-determination of the constant. After some hesitation, I decided upon carrying out this programme, and thanks to the indefatigability and youthful energy of my excellent collaborator, the work was completed in less time than I thought it would demand.—W. D.

(To be continued).

MANURIAL EXPERIMENTS WITH TURNIPS.*

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THE experiments about to be described were carried out in 1889, and had for their object the testing of the value of basic slag as a turnip manure. In order to make the results as valuable as possible, the experiments were carried out on farms in different parts of the West of Scotland; and the author would take this opportunity of expressing his great indebtedness to those gentlemen who so kindly co-operated with him in carrying them out, and for the time and trouble they were good enough to place at his disposal. It is quite unnecessary to say a single word in explanation of what basic slag is. Most farmers have heard a good deal during the last year or two regarding it. The very successful results obtained by its use on the Continent—especially in Germany—have drawn the attention of many of our farmers to its claims as a valuable source of phosphatic manure. But the British farmer is a cautious man, and the mere fact of a manure finding favour with the German farmer is, of itself, not sufficient guarantee to his mind to warrant him following suit. This caution is undoubtedly commendable. No farmer ought certainly to use a manure he is not convinced will repay him. He ought, however, to endeavour to ascertain the value of any great new source

of manure as soon as possible. Unfortunately the opportunities and facilities he enjoys for testing the value of new manures are in this country not so numerous as are desirable, and the ultimate result of this extreme caution may be that a cheap and valuable manure may be allowed to be neglected, or it may be sent abroad for use there.

The rapidity with which basic slag found its way into the German agricultural markets was undoubtedly due to the fact that the German farmer, unlike the English farmer, enjoys exceptional advantages, in the facilities he possesses, for having any new manure tested. Germany, with its magnificently equipped experimental stations scattered throughout the length and breadth of the land, is not long in providing herself with the desired information.

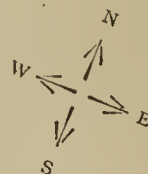
When we consider that basic slag is chiefly produced in this country, that it is to be had in very large quantities and at a very moderate price,* it does seem highly desirable that in the interests of our agriculture very many more attempts should be made to ascertain whether it really is a cheap and valuable form of phosphatic manure for our British soils, and whether it is in our interests to allow it to be entirely exported to Germany instead of using it ourselves.

The slag used in these experiments was of quality, so far as I am aware, hitherto unexperimented with, except in North Wales, where it was used last year at my suggestion in some experiments carried out by my friend Professor Dobbie, of Bangor. It contained of phosphoric acid only 8.55 per cent (=tricalcic phosphate of lime, 18.66 per cent), and its mechanical fineness was such that 56 per cent passed through the regulation sieve. The price of this slag would be, I am informed by the makers, so cheap that if it is shown to possess any fair manurial value, it would be for the farmer an extremely cheap source of phosphoric acid.

The experiments were intended to be carried out on the same scale in each of the series, but owing to circumstances a slight difference exists in certain cases. The aim of the experiments was to test the slag, first, alone in different quantities, and against superphosphate; secondly, with farmyard manure as against "super" and farmyard manure; and thirdly, with farmyard manure and nitrate of soda, as against super and nitrate of soda with farmyard manure; and the whole of the unmanured plots were tested against plots which received no manure.

The superphosphate and nitrate of soda, used in all the experiments, were the same. The superphosphate contained 29.62 per cent "soluble" phosphate; while the nitrate of soda contained 95.95 per cent nitrate of soda.

1	a	3	c	5	e	7	g	9	i
2	b	4	d	6	f	8	h	10	j



The first series of experiments were those carried out on the farm of Mr. John Gilchrist, of Orbiston Mains, Bellshill, Lanarkshire, to whom any value the experiments possess is largely due.

The experiment plots were twenty in number, situated near the centre of a large field with a good exposure, and

* From the *Transactions of the Highland and Agricultural Society of Scotland*.

* We should be able to purchase it cheaper than the Germans do, who so largely export it from this country.

well removed from any hedge. The plots were arranged in two rows, ten plots in each row. Ten of the plots measured each the 1·20th of an acre, while the other ten were each 1·480th of an acre. The latter ten plots received no manure, and lay between the manured plots. The object of having so many was to minimise as much as possible errors due to the natural inequalities of the soil.

The accompanying diagram will serve to show the arrangement of the plots.

The breadth of each plot was six drills, equal to about five yards. The soil is described by Mr. Gilchrist as "deep and alluvial on the south-east plots (viz., Nos. 1 and 2), somewhat stiffer on the middle plots, and on the north-west plots looser and more friable." The field, I should add, slopes to the south-east. The following is Mr. Gilchrist's statement of the history of the field during the previous five years in respect to the manures applied and crops grown:—

Year.	Crop.	Nature.	Manure.
1883.	Potatoes.	Of good quality.	Farmyard manure.
1884.	Wheat.	Heavy crop.	Nothing.
1885.	Hay.	Good crop.	Nothing.
1886.	Hay.	Heavy crop.	Police manure.
1887.	Hay.	Fair crop.	{ 1 cwt. nitrate of soda and 1 cwt. salt per acre.
1888.	Oats.	Extra heavy crop.	Police manure.

The plots were manured as follows:—

Nos. *a, b, c, d, e, f, g, h, i, j*, received nothing.

No. 1 received *basic slag* at the rate of 14 cwt. per acre.

No. 2 received *superphosphate* at the rate of 9 cwt. per acre.

No. 3 received *basic slag* at the rate of 7 cwt. per acre.

No. 4 received *superphosphate* at the rate of 4½ cwt. per acre.

No. 5 received *basic slag* at the rate of 14 cwt. per acre, and *farmyard manure* at the rate of 20 tons per acre.

No. 6 received *superphosphate* at the rate of 7 cwt. per acre, and *farmyard manure* at the rate of 20 tons per acre.

No. 7 received *superphosphate* at the rate of 4½ cwt. per acre, *farmyard manure* at the rate of 20 tons per acre, and *nitrate of soda* at the rate of 1 cwt. per acre.

No. 8 received *basic slag* at the rate of 7 cwt. per acre, *farmyard manure* at the rate of 20 tons per acre, and *nitrate of soda* at the rate of 1 cwt. per acre.

No. 9 received *basic slag* at the rate of 14 cwt. per acre, *farmyard manure* at the rate of 20 tons per acre, and *nitrate of soda* at the rate of 1 cwt. per acre.

No. 10 received *farmyard manure* at the rate of 20 tons per acre.

The experiments were carried out with *Aberdeen yellow turnips*, which were sown on the 21st of May, during favourable weather, and which braided well. All the manures, with the exception of the nitrate of soda, were spread, or sown in the drills along with the seed. The farmyard manure was spread in the bottom of the drills, the slag and the superphosphate put on the top of it. The drills were then covered and sown the same evening. The nitrate of soda was applied as a top-dressing on the 12th of July (*i.e.*, some seven weeks after sowing). The weather after sowing was pretty dry. The crop was entirely free from turnip-fly.

When visited on the 26th of July the plots which had received dung showed best, but between the remaining plots there seemed to be very little apparent difference. The slag seemed to tell best on the *lightest* soil. Mr. Gilchrist informed me that the plots which did not receive dung were some fourteen days later in being singled than the plots which did. The moisture carried into the drills along with the dung evidently helped the germination of the seed.

The turnips were lifted and weighed on the 18th of November. The following were the results. The weights do not include tops, which were not weighed.

I shall give the yield of the nothing plots first of all.

No.	Tons.	Cwt.
<i>a</i>	18	17
<i>b</i>	14	0
<i>c</i>	14	11
<i>d</i>	9	8
<i>e</i>	14	2
<i>f</i>	14	2
<i>g</i>	17	11
<i>h</i>	15	0
<i>i</i>	12	17
<i>j</i>	13	5
Total	143	13

giving an average of 14 tons 7 cwt.

The discrepancy in the results of these nothing plots strikingly exemplifies the necessity of taking into account the inequalities in the soil, and the peculiar difficulties in the way of arriving at satisfactory results in this kind of experimentation.

The results of the manured plots are as follows:—

No.	Manure.	Yield of turnips per acre.		Increase over nothing plots	
		Tons.	Cwt.	Tons.	Cwt.
1.	14 cwt. slag	21	10	+ 7	3
2.	9 cwt. super	18	5	+ 3	18
3.	7 cwt. slag	13	5	— 1	2
4.	4½ cwt. super	11	15	— 2	12
5.	14 cwt. slag, 20 tons dung..	22	5	+ 7	18
6.	7 cwt. super, 20 tons dung .	22	0	+ 7	13
7.	4½ cwt. super, 20 tons dung, 1 cwt. nitrate of soda ..	24	10	+ 10	3
8.	7 cwt. slag, 20 tons dung, 1 cwt. nitrate of soda ..	24	10	+ 10	3
9.	14 cwt. slag, 20 tons dung, 1 cwt. nitrate of soda ..	25	10	+ 11	3
10.	20 tons dung	22	10	+ 8	3

The above results call for some remarks. In the first place it will be noticed that plots Nos. 3 and 4, respectively manured with 7 cwt. of slag, and 4½ cwt. of super, instead of showing an increase over the nothing plots, show a decrease of 1 ton 2 cwt. in the one case, and 2 tons 12 cwt. in the other. In noticing this I was first inclined to think that the inequality in the yield of the nothing plots might explain it. I find, however, that on looking at the nothing plots adjoining these two plots, while in the case of No. 4 they do help to explain the anomaly, in the case of No. 3 they, on the other hand, increase it. With regard to the other plots it will be seen that No. 9 shows the largest increase, viz., 25 tons 10 cwt., or an increase over the average of the unmanured plots of 11 tons 3 cwt.,—*i.e.*, an increase of over 77 per cent. This plot, as will be seen from the table, was manured with 14 cwt. slag, 20 tons dung, and 1 cwt. of nitrate of soda per acre. The plots which show the next largest increase are Nos. 7 and 8, viz., 24 tons 10 cwt., or an increase over the average of unmanured plots of 10 tons 3 cwt.—*i.e.*, about 70 per cent of an increase. These plots received the same quantities of dung and nitrate of soda as No. 9, and 4½ cwt. of super, and 7 cwt. of slag respectively.

In summing up these results, and attempting to draw some practical conclusions from them, we may estimate the money value represented by the increase of crop obtained by the use of the manures; then calculate the money value of the manures applied, and by deducting the latter from the former, ascertain what the profit amounts to. Secondly, we may estimate the unitary value these experiments show phosphoric acid to possess

in the form of basic slag and superphosphate respectively. The following table shows side by side the cost of the manures and the value of the increase in crop. The slag is calculated at £1 per ton, the super at £2 15s. 6d., the nitrate of soda at £10 per ton, and the dung at 6s. per ton:—

No.	Manure.	Cost.	Value of increase of crop.
1.	14 cwt. slag	£0 14 0	£5 0 0
2.	9 cwt. super	1 5 0	2 15 0
5.	14 cwt. slag and 20 tons dung	6 14 0	5 11 0
6.	7 cwt. super and 20 tons dung	6 19 0	5 6 0
7.	4½ cwt. super, 20 tons dung, and 1 cwt. nitrate of soda.. ..	7 2 0	7 2 0
8.	7 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda.. ..	6 17 0	7 2 0
9.	14 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda.. ..	7 4 0	7 16 0
10.	20 tons dung	6 0 0	5 14 0

N.B.—The turnips were sold for 14s. a ton.

From the above figures it will be seen that the only plots showing a clear profit are Nos. 1 and 2, which received slag and super alone. In the case of plots Nos. 8 and 9, which received dung and nitrate of soda in addition, there is, it is true, a slight profit; while in the case of No. 7 the cost of the manures and the value of the increase of crop balance each other. It will be seen in this case that the dung applied in such large quantities does not repay itself. Of course it must be borne in mind that the effect of the dung will not merely be felt during the first year, but also throughout most of the rotation. Still, while this is doubtless true of the dung, it may also be argued that it is likewise true to a certain extent of the slag.

On the whole, therefore, it would seem that the application of farmyard manure in such large quantities is not economical. Comparing plots Nos. 1 and 10, which received 14 cwt. slag and 20 tons dung respectively, we find that the increase in crop is practically the same, although the difference in the cost of the manures applied amounts to £5 6s.

A comparison of plots Nos. 5, 6, and 10 shows that even an application of 20 tons of farmyard manure alone constitutes in this case an excessive mineral manuring, since the addition of 14 cwt. slag and 7 cwt. super respectively produces no increase. That, however, this does not apply to the same extent to nitrogen, plots Nos. 7 and 8 seem to indicate. In the case of these two plots it will be seen that the addition of 1 cwt. of nitrate of soda increased the value of the yield nearly £2 per acre.

In conclusion, it must be admitted that the value of these experiments is considerably impaired by the fact that the rate at which the manures have been applied is excessive. As, however, many farmers apply manures very much on the same scale, these results cannot fail to possess considerable interest for many.

The next series of experiments were carried out on the farm of Mr. George Graham, Easterboard, Croy, in the county of Dumbartonshire. The experiments were carried out on a clayey soil, and each plot was one-tenth of an acre in extent. The field possesses a fair southern exposure, the plots were each 2½ yards broad, consisting of three drills. They ran from north to south—to within 6 yards of the top of the field, where there is a very ragged hedge, and to the foot of the field, where there is a ditch, separating it from the adjoining field.

The soil is described by Mr. Graham as "rather clayey, with a white moorish sand in it; altogether a poor soil, and has always required very liberal treatment to raise good crops." A carefully selected sample of the soil was

analysed before the commencement of the experiments; and the following are the results:—

(a) Mechanical analysis—

Clay	79.91 per cent
Sand	20.09 „

100.00

(b) Chemical analysis (soil dried at 212° F.)—

Organic matter*	10.633
Iron sesquioxide and alumina.. ..	9.000
Lime	0.504
Magnesia	0.366
Potash.. ..	0.141
Soda	0.307
Sulphuric acid	0.078
Phosphoric acid.. ..	0.185
Insoluble siliceous matter, chlorine, carbonic acid, &c... ..	78.786

100.000

* Containing nitrogen 0.232.

The past history of the field is described by Mr. Graham as follows:—"It was green cropped in 1880 with turnips, and got liberal manuring (25 to 30 tons), with City of Glasgow police manure. The crop of turnips was very poor; but the succeeding oat crop was fair, and the hay crop in 1882 was also a fair crop. In the summer of 1883 it was eaten by cattle till the middle of June, and then left to grow hay, which was mown about the end of July.

It has been in grass ever since, till last year, when there was a crop of oats on it, which was poor, with the exception of a small piece at the top of the field, which was good." I forgot to add that, with regard to the situation of the field, the north side is a very little higher than the south, and that a slight elevation takes place two-thirds of the way down the field, so that one part lies to the south and another to the north. As, however, each plot extends the whole length of the field, this inequality is shared equally by every plot.

The field was deeply ploughed with Oliver's chilled plough about the end of November. It was wrought into a fine tilth just before drilling. The drills were opened on the 27th of May, the farmyard manure spread in, and the slag, superphosphate, and the nitrate of soda were sown with the hand the same day. The drills were then closed, and the turnips were sown the following morning before seven o'clock, rain beginning to fall before the sowing was finished. The ground was in good order, and other circumstances were favourable—rain and heat continuing for several days. The kind of turnip used in this experiment was Drummond's Improved Aberdeen Green Top Yellow. The following is a statement of the quantities of manures applied per acre:—

Plot No.

1. Nothing.
2. 4 cwt. super.
3. 8 cwt. super.
4. 6 cwt. slag.
5. 12 cwt. slag.
6. Nothing.
7. 6 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda.
8. 6 cwt. slag and 15 tons dung.
9. 12 cwt. slag and 15 tons dung.
10. 12 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda.
11. Nothing.

The following are the notes supplied me by Mr. Graham:—"June the 5th. The turnips braided; the ground at that time being very much battered with rain, and caked on the top. At the end of June the turnips were thinned—all, at any rate, with the exception of No. 1 (nothing plot), which was not ready for thinning till the 11th of July. On that date the plots showed as follows:—

Nos. 7 and 10—those which received slag along with dung and nitrate of soda—looked best.

Plots Nos. 8 and 9—those which had received, along with the slag, dung—were next best in appearance, and only slightly inferior to Nos. 7 and 10.

Plots Nos. 2 and 3—those which had received superphosphate in larger and smaller quantity respectively—came next in order, looking considerably poorer, but differing very little from one another.

Plots Nos. 4 and 5—those which had received slag in larger and smaller quantity respectively—came next in appearance, and did not seem to differ in appearance from one another.

Plots Nos. 6 and 11—those which received nothing—came last." With regard to these two plots, Mr. Graham remarks that they each received a small portion of the slag which was blown over, when being sown in the adjoining plots, and that they can scarcely be regarded as "fair" nothing plots.

(To be continued).

NOTICES OF BOOKS.

Our Secret Friends and Foes. (Expanded from Lectures delivered before Popular Audiences in London, Edinburgh, and elsewhere). By PERCY FARADAY FRANKLAND, Ph.D., B.Sc., F.R.S., F.C.S., &c. Society for Promoting Christian Knowledge. London: Northumberland Avenue. 1893. Pp. 167.

For a long time the intelligent part of the public has felt the want of a manual of bacteriology, popular, yet at the same time accurate, and on a level with the present state of Science. Dr. P. F. Frankland has most ably supplied this want, and has thereby rendered a serious service to Science in general and to hygiene in particular. The notions of the public concerning bacteriological research and its possible results have been hitherto hazy in the extreme. It has been made the subject of pointless jokes by the "witling gallants" of the literary and the political press. It has been execrated by mœnads and zœophilists, and it is even yet slighted by a few physicians of eminence who owe their success, in fact, to what may be called "rule of thumb,"—a certain incommunicable tact. To all these classes of gainsayers Dr. Frankland offers valuable lessons, if his readers will only take them to heart.

The author gives us first a general account of the structure and the classification of these ultra-microscopic organisms, bacilli, spirilla micrococci, collectively spoken of as *bacteria* as well as the *yeasts* and the *moulds*. He describes the formation of spores—the reproductive forms of many species,—justly characterised as the hardest forms of living matter which Science has yet revealed, since they are "unaffected by cold far greater than that of an Arctic winter," and can sometimes even survive a few minutes exposure to boiling water.

The second chapter is devoted to the micro-organisms of the air, and involves an account of the long controversy on the alleged "spontaneous origin of life," or abiogenesis. The controversy was finally decided by Pasteur and Tyndall in such a manner as to fully confirm the aphorism of Hunter, "Omne vivum ex ovo." Dr. Frankland duly calls attention to the comparative paucity of microbes at great altitudes, on sea at great distances from land, and in undisturbed air. Mention is made of *Bacillus prodigiosus*, which sometimes turns bread of a blood-red colour, and occasioned in the dark ages the dreaded portent of the "bleeding host," sometimes used as a pretext for the immolation of Jews, witches, and heretics. The study of the air-dwelling micro-organisms is mentioned as having led the way to Sir Joseph Lister's great discovery,—the antiseptic treatment of wounds.

We come next to the micro-organisms of water. Here are described the surprising results of filtration. The

importance of drinking-water in reference to public health is truthfully asserted to have been first established and taught in Britain, even before the microbial theory of disease was established.

"Useful Micro-organisms" is the title of a highly instructive chapter. Passing over the part played by certain *Saccharomyces* in the production of alcohol—a function which certain reformers think is a mistake in creation—we come to the question of nitrification, *i.e.*, the conversion of the inert nitrogen of the air into nitric acid, in which state it becomes available as plant-food. In discussing the fixation of nitrogen we find no mention made of the researches of M. Georges Ville, who certainly has taken no unimportant share in demonstrating the action of atmospheric nitrogen in the nutrition of vegetables.

It is curious that the two bacteria which respectively convert ammonia into nitrous acid and nitrous acid into nitric acid, require a culture-medium of silica in the gelatinous state. This little fact may yet be found to have an unimagined importance. The author considers that at the epoch when the nitrate beds of Chili and Peru were formed, the nutrifying organisms were much more powerful than those now existing.

Micro-organisms are shown to be gradually assuming the character of chemical reagents. At the same time Dr. Frankland shows two things: That among members of a "pure culture" there may be individual differences, and that they may be modified by cultivation. Here the author writes under Darwinian inspiration, and finds one of the most interesting evidences of Evolution, as it has been experimentally shown by Dr. Dallinger, F.R.S.

We next come to the malignant or pathogenic organisms, the producers of cholera, typhoid, small-pox, diphtheria, rabies, and doubtless of all the communicable diseases. Prominent mention is made of the infectious character of pulmonary consumption. It is a sad fact that an Australian physician who anticipated Koch in this striking discovery reaped in return, not honours but something very like persecution. The populace of Melbourne was enraged at being told that their climate was not a specific for tubercular disease.

The bacillary character of tetanus or lock-jaw, established by Kitasato, a Japanese pupil of Prof. Koch, is of the greatest importance. A case is mentioned of a child dying of tetanus in consequence of some cobwebs having been applied to stop the bleeding from a cut. Spores of tetanus had become entangled in the web, and had set up the dreadful infection. The tetanus bacillus haunts garden soil, the mud of swamps, &c. Hence we need not wonder that tetanus ensues upon wounds received from the arrows of certain African and Oceanic savages. The points of the arrows are poisoned by dipping them in the mud of swamps and allowing them to dry in the sun.

This chapter is aptly closed with an expression of regret that in the development of preventive medicine England has unfortunately lagged behind, as it is all but impossible at the present time to carry out the necessary investigations in this country. No names are mentioned, whether of individuals or of organisations, but it is impossible to mistake the allusion. We hope that Dr. Frankland is not mistaken in his confidence that the public mind is beginning to recover from the hysterical delusions with which it has been "chloroformed."

One of the lessons of this book is the exceptional fruitfulness of boundary lines. The study of the micro-organisms lies on the mutual frontiers of biology and chemistry, and its cultivation has proved most remunerative. We trust that this invaluable book will receive the wide and thorough appreciation which it merits.

The Framework of Chemistry, Part I. Typical Facts and Elementary Theory. By W. R. WILLIAMS, M.A. London: G. Bell and Sons. 1892. Pp. 48, 8vo.

THIS little book would be very useful if it had not quite so many predecessors in the same field. It has one

creditable peculiarity which should not be overlooked; it is not written down to the requirements of students preparing for any examination.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 3, January 16, 1893.

Phosphorescent Zinc Sulphide considered as a Photometric Standard.—Charles Henry.—Within wide limits, and consequently under conditions easy to be realised, the quantity of light emitted by phosphorescent zinc sulphide at a given moment is independent of the distance of the magnesium, independent of the time of illumination, independent of the thickness of the layer of sulphide. In a word, phosphorescent zinc sulphide presents in the highest degree the characters required by a secondary photometric standard.

An Acid Potassium Platonitrite.—M. Vèzes.—A solution of potassium platonitrite slightly acidulated with any acid occasions after a certain degree of concentration a dark red deposit on the sides of the vessel, consisting of fine crystalline needles, slightly soluble in cold water, but soluble with a yellow colour in hot water. Its composition is $\text{Pt}_3\text{O}(\text{NO}_2)_6\text{K}_2\text{H}_4 + 3\text{H}_2\text{O}$. Hence the red salt is the acid bipotassium salt of an unknown hexabasic acid.

The Decomposition of Chloroform in Presence of Iodine.—A. Besson.—The decomposition of chloroform at incipient redness in presence of iodine yields as principal products C_2Cl_4 35 per cent (or 20 per cent on the chloroform employed), C_2Cl_6 20 per cent, and as secondary products CCl_4 15 per cent, C_6Cl_6 10 per cent, C_4Cl_6 8 per cent: the remnant consisting of small quantities of products not separated comprising traces of iodine compounds and a little C_2HCl_5 .

Some Ethers of Homopyrocatechine.—H. Cousin.—Homopyrocatechine forms two methylic ethers, two ethylic ethers, a methylethyl ether, and a diacetic ether.

Determination of Phosphorus in Irons and Steels.—Adolphe Carnot.—This paper will be inserted in full.

The Waste of Nitrogen from Farmyard Manure.—A. Muntz and A. Ch. Girard.—The authors find that peat litter retains nitrogen better than does straw. The additions to straw litter of copperas and of gypsum do not appreciably reduce the loss of nitrogen. One reason of this is the quantity of fixed bases, alkaline or alkaline-earthly, contained in the excreta of farm animals, especially of horned cattle and sheep. This alkaline matter decomposes the ferrous sulphate to such an extent that at least 700 kilos. of the ferrous salt would be required yearly per head of horned cattle to arrest the escape of ammonia.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 5.

An Improved Calorimeter.—F. Fischer (*Zeit. Angew. Chemie*).

An Automatic Sprengel-Pump.—H. T. Wells (*Ber. Deut. Chem. Gesell.*).—Both these papers are useless without the accompanying figures.

Agitating Machine for the Analysis of Superphosphates.—O. Güssefeld (*Zeit. Angew. Chemie*).—This note requires the accompanying figures.

Blast for Carburetted Air.—M. Pauquelin (*Comptes Rendus*).

The Preservation or the Purification of Some Reagents.—W. Hampe (*Chem. Zeit.*).—As regards the preservation of hydrofluoric acid in bottles, &c., of vulcanite, the author states that organic substances may easily be taken up by the acid from the material of the bottles, so that after some time it distinctly decolorises solution of permanganate. In determining ferrous oxide in silicates, this circumstance may render the results too high. Hampe, therefore, for such determinations, recommends a previous addition of sulphuric acid and permanganate until a permanent red colour appears, after which the acid may be safely used. Hydrofluoric acid also takes up alkalies from some kinds of vulcanite. To avoid both these impurities, Hampe uses platinum bottles holding about 1 kilo., which, as a protection against injuries, are inclosed in a closely fitting copper flask, closed with a screw. For preparing non-arsenical sulphuretted hydrogen, Hampe, in case of ordinary analyses, considers it sufficient to cause the gas to traverse two or three receivers, containing either soda or sodium sulphide. In very accurate operations, Hampe obtains sulphuretted hydrogen from pure crystalline sodium sulphide and dilute sulphuric acid (1:10) which has been tested in Woolf's apparatus. The solid salt, along with a little water, is placed in a Woolf's bottle of medium size, one tubulure of which has a funnel tube fitted with a cock, whilst the other tubulure admits the gas-delivery pipe. The dilute sulphuric acid is introduced through the funnel tube in suitable quantity. The gas traverses a washing bottle of pure water or a solution of soda. In order to remove hydrochloric acid from chlorine gas (important in Woehler's process for determining total carbon in iron), Hampe uses a watery solution of permanganate, and allows the gas to traverse the washing liquor in small bubbles. The colour shows whether it is fit for use. The washing bottle is placed between the generating-vessel and the drying apparatus.

An Indicator in Alkalimetry.—Werner Bolton (*Zeit. Angew. Chemie*).—Especially in cases where the operation has to be performed by workmen, the author instead of dyes, which change colour, uses a concentrated solution of flower of sulphur in an alkaline sulphide. Of this solution a drop is added, and a corresponding quantity is deducted from the total acid consumed, or the liquid is stirred with a glass rod which has been dipped in the solution of alkaline sulphide. The solution is heated to ebullition and titrated. As soon as a milkiness appears in the liquid, which does not disappear on vigorous agitation, the operation is complete. The indication is better marked than that with litmus or turmeric.

The Analysis of Ferrochrome, Ferroaluminium, Ferrotungsten, Ferrosilicon, and Ferrotitanium.—A. Ziegler (*Dingler's Jour.*).—Already inserted.

Analysis of Galena and Lead Sulphate.—Rudolf Benedikt (*Chem. Zeitung*).—The decomposition of galena can be easily and completely effected by heating with hydriodic acid. The pulverised mineral is covered with some water in a hemispherical porcelain capsule, and then with a few c.c. of commercial hydriodic acid of 1.7 specific gravity. If the moistening with water is omitted there ensues a violent effervescence. The capsule is covered with a watch glass and heated on the water-bath. In a few minutes the lead sulphide is completely converted into lead iodide. The watch glass is removed, rinsed off, and evaporated to dryness. The residue when cold is covered with dilute nitric acid, the capsule is covered and heated on the water-bath. The nitric acid decomposes the lead iodide, with liberation of iodine. As soon as the oxidation is at an end the capsule is uncovered, the contents evaporated to dryness, the residue is moistened with dilute nitric acid, filtered, and washed out, when the entire lead is in solution as lead nitrate, and may be determined with sulphuric acid in the usual manner.

Lead sulphate is converted into lead nitrate in a similar manner. The substance is covered with a little water in a small beaker, hydriodic acid is added, and a moderate heat applied. In a few minutes the whole is reduced. Sulphur is deposited on the sides of the beaker. When cold, the contents of the beaker are washed with cold water into a capsule, evaporated to dryness, moistened with nitric acid, and further treated as above.

Process for the Quantitative Separation of Silver and Lead.—R. Benedikt and L. Gaus (*Chem. Zeit.*).—Already inserted.

Volumetric Determination of Sulphuric Acid by the Chromate Method.—K. Farnsteiner (*Chem. Zeit.*).—Already inserted.

Some Reactions of the Three Isomeric Amido-benzoic Acids.—Oechsner de Coninck.—(From the *Comptes Rendus*).

The Execution of Elementary Analyses by Combustion with Oxygen at High Pressure in the Calorimetric Bomb.—Prof. Berthelot.—(From the *Comptes Rendus*).

Saponification of Oils and Esters by Sodium Alcoholate.—K. Obermüller.—A. Kosei and K. Obermüller have formerly observed that as a rule the soda-soap of the existing acid and the free alcohol of the ester are formed. On further studying this process, Kosei and Krüger recognised as intermediate products the compound of the acid existing in the fat with the alcohol of the alcoholate employed, that is the ethyl- or amyl-ester. Latterly K. Obermüller has resumed the subject, and concludes that on assuming that the water present takes part in the reaction, the entire process may be easily explained. The sodium alcoholate forms at first with the glyceride of the fatty acid sodium glycerin and fatty ester. In presence of water the sodium glycerin is decomposed into glycerin and sodium hydroxide, which latter saponifies the ester, forming soda soap and alcohol.

Determination of the Carbonyl Oxygen of the Aldehyds and the Ketones.—H. Strache (*Monatshefte für Chemie*).—This paper requires the two accompanying illustrations.

The Determination of the Strength of Aqueous Solutions of Acetic Acid by means of the Specific Gravity.—E. Nickel (*Chemiker Zeit.*).—This operation presents a certain difficulty, as the specific gravity of such solutions increases with augmenting concentration only up to 80 per cent, and then decreases. The author overcomes this difficulty by determining the spec. grav. as usual, diluting with water, and determining the spec. grav. again. If the spec. grav. rises, the higher value must be assumed to be correct, but if it falls, the lower.

The Determination of the Acidity of Milk.—H. C. Plant (*Archiv. für Hygiene*).—Already inserted.

Examination of Vinegar.—S. A. Vasey.—(From the *CHEMICAL NEWS*).

Recognition of Bombay Mace.—Th. Waage and O. Warburg.—The microchemical reaction with potassium chromate is recommended.

Process for Examining Commercial Spirits.—Ed. Mohler (*Ann. Chim. Phys.*).—Already inserted.

Examination of Safron and Safron Substitutes.—E. Vinassa (*Archiv. Pharm. Chemie*).—This process is of no practical importance.

The Determination of Kreatinine in Urine.—MM. Gautrelet and Vieillard.—Already inserted.

Method for Determining the Volume of the Corpuscular Elements of the Blood.—M. and L. Bleibtreu (*Pflüger's Archiv*).—Not adapted for useful abstraction.

Detection of Carbon Monoxide in the Blood.—H. Bertin-Sans and J. Moitessier.—(From the *Comptes Rendus*).

The Spectrum of Methæmoglobine.—P. Dittich and M. Araki (*Archiv. Experiment Pathol.*).—The spectrum contains only two absorption-bands. A solution of pure crystals, if examined in a stratum of 1 c.m. in depth, transmits the red rays up to the wave length of 660, even at a concentration of 3 per cent. Then follows the obscurity corresponding to the well-known methæmoglobine bands, the middle of which coincides with $\lambda = 632$. From these the absorption decreases to about 606, and remains then approximately constant as far as D, and then again increases. The next stage of darkening has its turning-point at 579, corresponding to the absorption band II. of authors. A further stage of darkening at about 540 occurs not as a band, but as the commencement of a strong diffused absorption, which increases uniformly and takes up the rest of the spectrum. The bands III. and IV. of former researchers, Dittich was unable to find in solutions perfectly free from oxyhæmoglobine.

Chemico-Toxicological Detection of Hydrastin.—Dioscoride Vitali.—He proposes two reactions. If a crystal of hydrastin or a salt of hydrastin is covered with $\frac{1}{2}$ to 1 c.c. of sulphuric acid in a porcelain capsule and stirred with a glass rod, the mass takes a yellow colour, which, on the addition of a granule of saltpetre and stirring with a glass rod, turns to a yellowish brown. If a solution of stannic chloride is added drop by drop, a splendid violet-red colour is produced. If hydrastin in a porcelain capsule is covered with four to six drops of nitric acid, the liquid is heated to boiling and allowed to evaporate at a gentle heat after expelling the nitrous acid. The yellowish residue is turned a dark green if touched with a drop of an alcoholic solution of potassium hydroxide. If the residue when cold is covered with sulphuric acid, it takes an intense violet colour.

A Revision of the Determination of the Atomic Weight of Copper.—Th. W. Richards (*Amer. Acad. of Art and Science*).—The mean referred to, $O = 16$, is $Cu = 63.604$.

MISCELLANEOUS.

Royal Institution.—On Thursday next, February 9, Professor Patrick Geddes will begin a course of Four Lectures on "The Factors of Organic Evolution"; and on Saturday week, February 18, The Right Hon. Lord Rayleigh will begin a course of Six Lectures on "Sound and Vibrations."

Explanation of the Difficult Solubility of Chemically Pure Zinc in Acids.—Jul. Weeren (*Ber. Deutsch. Chem. Gesell.*).—The author assumes that chemically pure zinc, as well as other chemically pure metals, are insoluble in acids because in the moment of their immersion in the acid they are at once enclosed by an atmosphere of condensed hydrogen, which under normal conditions prevents a further action of the acid. In proof of this assumption it is observed that if the atmospheric pressure is reduced the zinc is dissolved.

An Examination - Paper.—Some students having expressed a desire to know the correct answer to a recent paper, set for the Intermediate Medicine Examination of London University, a committee of teachers has, after much anxious consideration, ventured to suggest the following replies, in the hope that they may serve as a guide to others who may still have this examination before them.

Q. 1.—"If bottles were placed before you containing the following substances: (1) acetamide, (2) toluene, (3) phenol, (4) ethyl iodide, (5) ethylene bromide, (6) bromobenzene, how would you be enabled to identify each of them by noting their appearance, odour, and behaviour when poured into water? How would you demonstrate the presence of nitrogen in the acetamide, and of bromine in the bromobenzene?"

Answer.—This question divides into two main heads, viz., (a) How would you be enabled to identify certain substances? and (b) How would you detect nitrogen and bromine? (a) I should adopt one of three courses; I should either read some text-book, or, better, I should attend the lectures of some well-known teacher: or perhaps, best of all, I should ask a Fellow of the Institute of Chemistry. I should thus be enabled to identify the substances. (b) The presence of nitrogen in the acetamide is easily shown by boiling a sample with caustic soda and smelling the evolved ammonia, and of bromine in the bromobenzene by passing its vapour over red-hot lime, treating the mass with water, and testing for bromine by liberating it with chlorine water.

Q. 2.—“What is the nature of the experimental evidence which has led to the conclusion that tartaric acid is a dihydroxydicarboxylic acid?”

Answer.—The nature of the evidence is required. A dibasic acid is characterised by the existence of an acid, as well as of a neutral salt; the presence of hydroxyl groups is inferred from the formation of ethylic and acetylic derivatives, and from the fact that they may be substituted for bromine by the action of silver hydroxide, in a compound containing bromine, of which the constitution has been established.

Q. 3.—“The substance obtained by treating glycerol with nitric acid is commonly known as nitro-glycerin” (and commonly spelt with an “e”). “Why is this an incorrect name, and in what respects does the substance differ from a nitro-compound?”

Answer.—Before proceeding to infer conclusions it is well to verify premises; the committee therefore investigated the action of nitric acid on glycerin. A mixture of the two substances was made, and after a short time a torrent of red fumes was evolved. The committee then retreated to a convenient distance and focussed a cathetometer on the scene of action. The products were mostly gaseous; the residue contained a little oxalic acid. It assumed, therefore, that oxalic acid is the substance referred to. It is obvious that this body has no claim to the name nitro-glycerin, for it contains no nitrogen; and it may be distinguished from a nitro-compound by its reducing an acidified solution of permanganate.

Q. 4.—“How has glucose been prepared artificially? What is the difference in constitution between glucose and levulose?”

Answer.—The method of preparing artificially, or of manufacturing glucose, is by boiling rags or starch for some days with dilute sulphuric acid, neutralising the acid with lime, filtering from the gypsum, and concentrating in a vacuum pan. The one is an aldehyd containing the group CHO, and the other a ketone containing the group CO. (This question obviously refers to the synthesis of glucose; but the actual answer is the one given).

Q. 5.—“What is the distinction between fatty and aromatic compounds?”

Answer.—The distinction means, we presume, the chief distinction. The chief distinction between fatty and aromatic compounds is that they are described in different sections of the same text-book. Nowadays, so many ring-compounds are fatty, and so many chain-compounds mostly aromatic, that it may be stated that fatty compounds are aromatic, and that aromatic compounds are fatty.

Q. 6.—“Describe the manner in which you would effect the complete oxidation of the alcohol in a dilute aqueous solution, and in which you would separate the resulting acid and convert it into sodium salt. Sketch the apparatus you would use.”

Answer.—By complete oxidation is meant conversion into carbon dioxide and water. We know of no way of effecting this, except by means of a living organism, and of no organism so suitable for the purpose as that of an habitual toper. We would therefore suggest the following method. Take a toper, provided with an œsophagus, a stomach, intestines, a circulatory system, and lungs,

and inject the liquid through the mouth. This will not be difficult, if the alcohol be not too dilute ethyl alcohol. Methyl alcohol requires an habitual drunkard, who may be more difficult to procure. If the alcohol be one of the higher of the series, it may be necessary to inject some ethyl alcohol in considerable amount as a preliminary precaution. Let nature take its course; cause the toper to breathe into a bladder, and expel the expired gases through a solution of caustic soda until it is saturated. Evaporate the solution of sodium carbonate and ignite the residue. The apparatus used is termed a toper. He may be sketched thus:—

An occasional sip,
An habitual nip:
A continuous soak,
A thirst like to choke.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Medical, 8.30.

— Society of Arts, 8. “The Practical Measurement of Alternating Electrical Currents,” by Prof. J. A. Fleming, F.R.S. (Cantor Lectures).

— Society of Chemical Industry, 8. “Manufacture of Nitric Acid,” by Oscar Guttman. “Detection and Estimation of Lead in Citric and Tartaric Acids,” by R. Warrington. “New Form of Laboratory Filter-Press,” by C. C. Hutchinson.

TUESDAY, 7th.—Institute of Civil Engineers, 8.

— Pathological, 8.30.

— Royal Institution, 3. “The Functions of the Cerebellum, and the Elementary Principles of Psychophysiology,” by Prof. Victor Horsley, F.R.S.

— Society of Arts, 8. “Pottery Glazes; their Classification and Decorative Value in Ceramic Design,” by Wilton P. Rix.

WEDNESDAY, 8th.—Society of Arts, 8. “Some Points in the Chemical Technology of Oil Boiling, and New Process for Preparing Drying Oils,” by Prof. W. Noel Hartley, F.R.S.

— Geological, 8.

— Pharmaceutical, 8.

THURSDAY, 9th.—Royal, 4.30.

— Royal Society Club, 6.30.

— Mathematical, 8.

— Institute of Electrical Engineers, 8.

— Royal Institution, 3. “The Factors of Organic Evolution,” by Prof. Patrick Geddes.

FRIDAY, 10th.—Royal Institution, 9. “Some Associated Organisms,” by Prof. Charles Stewart, Pres. L.S.

— Astronomical, 3. (Anniversary).

— Society of Arts, 8. “The Development and Transmission of Power from Central Stations,” by Prof. W. Cawthorne Unwin, F.R.S.

— Physical, 5. (Annual General Meeting). “Recent Determinations of Molecular Refraction and Dispersion,” by Dr. J. H. Gladstone, F.R.S. “The Separation and Striation of Gases,” by E. C. C. Baly.

SATURDAY, 11th.—Royal Institution, 3. “Expression and Design in Music,” by Prof. C. Hubert H. Parry, M.A.

TO CORRESPONDENTS.

Cyanogen.—The paragraph is full of errors. We do not see the use of reprinting it in the CHEMICAL NEWS.

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THE CHEMICAL NEWS.

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ON A

16 FEB 93

METEORIC STONE FOUND AT MAKARIWA,
NEAR INVERCARGILL, NEW ZEALAND.*

By G. H. F. ULRICH, F.R.S., F.R.M.

Professor of Mining and Mineralogy in the
University of Dunedin, N.Z.

THE specimen described in this memoir was found in the year 1879 in a bed of clay which was cut through in making a railway at Invercargill, near the southern end of the Middle Island of New Zealand. Originally this meteorite appears to have been about the size of a man's fist, and to have weighed four or five pounds, but it was broken up, and only a few small fragments have been preserved. The stone evidently consisted originally of an intimate admixture of metallic matter (nickel iron) and of stony material, but much of the metallic portion has undergone oxidation. Microscopic examination of thin sections shows that the stony portion, which is beautifully chondritic in structure, contains olivine, enstatite, a glass, and probably also magnetite, and through these stony materials the nickel iron and troilite are distributed. The specific gravity of portions of the stone was found to vary between 3.31 and 3.54, owing to the unequal distribution of the metallic particles. A partial chemical examination of this meteorite was made by the author and Mr. James Allen, but the complete analysis has been undertaken by Mr. L. Fletcher, F.R.S., of the British Museum. The analysis, which when finished will be communicated to this Society, has gone so far as to show that the percentage mineral composition of the Makariwa meteorite may be expressed approximately by the following numbers:—Nickel iron 1, oxides of nickel and iron 10, troilite 6, enstatite 39, olivine 44.

FURTHER RESEARCHES IN CONNECTION WITH THE METALLURGY OF BISMUTH.†

By EDWARD MATTHEY, F.S.A., F.C.S.,
Associate of the Royal School of Mines.

IN 1886–87 and in 1890 I submitted papers to the Royal Society bringing under notice facts which had come to my knowledge whilst engaged upon the practical extraction of this beautiful metal from its ores, and in its separation from impurities which are always associated with it when in a crude or unrefined state.

IV.—Bismuth: Its Separation from Arsenic.

In a paper dated February 10, 1887 (*Proc. Roy. Soc.*, vol. xlix.), allusion is made to the fact that arsenic is often one of these impurities, and at the same time a method is given by which the separation of this metal from bismuth was then successfully effected.

The process adopted when that paper was read, and for a considerable period subsequently, when working upon bismuth containing arsenic, consisted in removing the arsenic by fusing the arsenical bismuth in contact with metallic iron at a dull red heat and under flux. A compound of iron and arsenic was thus formed and could be removed as a scum,—the disadvantages of this process being, first, loss of bismuth by volatilisation, and,

secondly, much loss of time in the manipulation of any large quantity to be treated.

Having occasion, a few months ago, to melt together a large quantity of arsenical bismuth, some 700 or 800 kilos., that is, more than three quarters of a ton, in order to obtain a homogeneous alloy upon which to work subsequently by the process above alluded to, it became evident that when the temperature was raised above the melting-point of bismuth, the surface of the metal being exposed to the atmosphere, arsenical fumes appeared, and that these increased as the temperature of the metal became more elevated, the result being that the arsenic came off in dense white fumes (As_2O_3).

The observation of this fact led to further experiments, and it was found that if the surface of the bath of fused arsenical bismuth was freely exposed to the air at a temperature rather higher than its own melting point, and if the molten metal was constantly stirred, it was possible to eliminate the whole of the arsenic alloyed with the bismuth by this simple process of fusion with stirring.

As it is a matter of considerable interest for metallurgists to know, not only that this elimination does take place, but also at what temperature it occurs, a series of experiments have been conducted with a view of determining this accurately.

The work of Roberts-Austen has shown that a thermo-junction is practically the only form of pyrometer that can be used for delicate thermal investigations of this kind, but the question arose which particular thermo-junction should be adopted. Was it well to use the platinum-iridium one as advocated by Barus, or the platinum-rhodium one suggested by H. le Chatelier? My previous work on the alloys of platinum and rhodium, lately published in the *Phil. Trans.*, settled the question in favour of the rhodium-platinum thermo-junction, for I was satisfied that the alloy of platinum with 10 per cent of rhodium is as homogeneous as any known alloy could well be, and is therefore admirably adapted for use as a thermo-junction, pure platinum being the opposing metal. Analysis proved that the alloy operated upon in these experiments contained 0.65 per cent of metallic arsenic.

It will be seen that the melting point of this alloy of bismuth is 278°C . By raising the temperature of the alloy to 395°C . the arsenic freely sublimates from the bismuth alloy, and at a temperature of 513°C . the whole of the arsenic is eliminated.

A point of much interest in relation to molecular physics became evident in the course of the investigation. Arsenic, as is well known, volatilises at the comparatively low temperature of 180°C ., without passing through the molten state. Arsenic is not, however, given off freely from the arsenical bismuth until a temperature of 395° is reached. So that the temperature of dissociation of this alloy, containing 0.65 per cent of arsenic, is 114°C . higher than the melting-point of the mass. It was interesting to determine at what temperature the arsenic would be evolved if the alloy were heated *in vacuo*.

A portion of the bismuth alloy containing 0.65 per cent of arsenic was introduced into a hard glass tube, slightly depressed to its centre, and connected at one end with a Sprengel pump, by which it could be rendered vacuous.

The pyrometric wires were in contact with the metallic alloy and passed to the galvanometer through the opposite sealed end of the glass tube.

Heat being applied, the first indication of the volatilisation of the arsenic, shown by the condensation of a film on the cool part of the tube, occurred at 275°C . When the alloy was quite melted the temperature indicated was 316°C .; arsenic came off freely when the temperature rose to 569°C ., condensing in a black mirror.

The metal was then allowed to cool, and its settling-point was found to be 268°C ., which corresponds with that of the melting-point of bismuth.

The bulk of the arsenic does not appear to be evolved *in vacuo* at a lower temperature than in air.

* Abstract of a paper read before the Royal Society, Feb. 2, 1893.

† Paper read before the Royal Society, January 26, 1893.

As regards the industrial application of the process, some ten to twelve tons of arsenical bismuth have already been treated in this very simple way, and it has been satisfactorily ascertained that there is no loss of bismuth by volatilisation with the arsenic.

V.—The Separation of Bismuth from Antimony.

The process hitherto adopted in practice for the separation of antimony from bismuth has usually consisted in a simple fusion at a dull red heat with bismuth oxide or bismuth "litharge"—an operation successful enough as to its results, but one requiring no small amount of skill in manipulation; it is also one by which only small quantities can be treated readily at one time—and moreover, the temperature which is necessary to effect the separation of the antimony involves appreciable loss on account of the volatilisation of the bismuth at a red heat; notwithstanding, many tens of tons of bismuth have, however, been treated under my direction by this process.

In an operation lately conducted, involving the melting of a quantity of bismuth containing about one per cent of antimony, it was found that a peculiar oily film was noticeable rising to the surface of the melted alloy; this film did not form all over the surface of the metal, but appeared to rise as from a boiling centre, and this although the metal was at a temperature very little above its melting-point. A portion of the film or layer was removed and tested in order to ascertain its nature, and it was found to contain a very appreciable proportion of *antimony*. I therefore caused the operation to be continued, stirring the metal from time to time with a dried wood stirrer. In the course of three or four hours, removing the film from time to time, the surface of the melted metal assumed a much brighter appearance, and on carefully testing it at this point, the metal was found to be *absolutely free from antimony*. To confirm this and to ascertain more exactly the conditions under which this separation takes place, a further quantity of impure bismuth was operated upon in a similar manner. This second quantity contained other impurities besides antimony, its analysis being as follows:—

Bismuth, by difference	96.20
Antimony	0.80
Tellurium	0.40
Lead	2.10
Copper	0.50
Arsenic	traces

100.00

The same simple process of fusion and stirring was again adopted—the quantity being about 350 kilograms.—and when the same oily film commenced to rise to the surface, the temperature of the molten mass of the alloy was taken by means of the *le Chatelier* pyrometer. A portion of the film removed showed, on being tested, a percentage of over 30 per cent of antimony. A slightly perceptible fume of arsenic was apparent as volatilising, so proving what I found to be the case in the separation of arsenic by simple fusion. (See *ante*).

The point at which this separation of antimony occurs was found to be about 350° C., and at this temperature the metal was maintained for about five hours.

The evidence of an oxidising action became now much less, and, although a very small amount of antimony was present, there was still a little remaining in the alloy; the temperature, therefore, was slightly raised and maintained at 458° C., as shown by the pyrometer, for about four hours, at the end of which time the bismuth became absolutely free from antimony.

The form in which the antimony separated was peculiar—a transparent glass, consisting of antimony oxide—containing about 10 per cent of bismuth; but, of course, in the removal of the antimony oxide a small proportion of the bismuth was mechanically carried with it, resulting

in the production of several very interesting and very beautiful metallurgical specimens.

The great advantage of this process is,—like that of the foregoing separation from arsenic,—its extreme simplicity, the low temperature which renders it possible to work upon very large quantities at one time, and the very small amount of time necessary for this separation in comparison with the process hitherto adopted, and the absence of loss in the bismuth operated upon by volatilisation. It is obvious that where metals can be so easily treated in large quantities, the labour and skill hitherto necessary is very considerably reduced, and there is the additional advantage that the loss attending large operations is minimised.

In this and in my previous papers upon this beautiful metal bismuth, I have been able to point to simple dry processes for its separation from gold, lead, copper, arsenic, and antimony, and all these processes are available for treating with care large quantities at one time. When it is remembered what is involved in having to dissolve any quantity of bismuth in acids, and its subsequent precipitation from solution, it surely will be admitted that much of the difficulty in purifying crude bismuth has been effectively removed, as the methods given have been found possible in practice, and advantageous.

ON THE ORIGIN OF COLOUR.

II. THE COLOUR SCALE. THERMO-RELATIONS. THE LAW OF COLOUR.

By WILLIAM ACKROYD.

(Continued from p. 27).

THE question has been asked why a colour scale should be used, and not the spectroscope, in investigations concerning the origin of colour?

A metachromatic scale produced by heat exhibits a natural sequence of colours which are of the same kind as those of bodies to be compared in investigations on the origin of colour. This is its first and most important claim for use to that purpose; it is an expression of colour evolution. I have shown that the changes of colour which it typifies are produced by a gradual and increasing absorption of the less refrangible rays (*Phil. Mag.*, Dec., 1876), and as some of these differences, which are readily appreciated by the eye, are not discernible with the spectroscope, eye observations, of which the colour scale is a record, are preferable to spectroscopic for a comparative study of colour in its relation to chemical constitution. It is well, indeed, it is so, as many of the bodies to be studied are amorphous, opaque, and insoluble in liquids without chemical change. What I take to be the true province of the spectroscope in this investigation will be shown in another paper.

The thermo-relations concerned in these colour changes are of interest, seeing that colour is determined to some extent by temperature. From Neumann's law it follows that *g*rm. molecules of a natural series of compounds containing the same number of atoms will require the same quantity of heat to raise them from absolute zero to the normal temperature. Thus the calories required to bring *g*rm. molecules of the following chromates from 0° to 273° absolute temperature will be—

	Calories.
Lemon-yellow, MgCrO_4 ..	$\frac{28.8 \times 273 \times 140}{140} = 28.8 \times 273$
Yellow, ZnCrO_4	$\frac{28.8 \times 273 \times 181}{181} = 28.8 \times 273$
Orange-yellow, CdCrO_4 ..	$\frac{28.8 \times 273 \times 228}{228} = 28.8 \times 273$

Or generally, if *a*, *b*, and *c* are the atomic heats of the elements in a natural series of compounds, and *m'*, *m''*,

Metachromic scale.	White.	Blue.	Green.	Yellow.	Orange.	Red.	Brown.	Black.
I. Binary compounds..	—	—	PtCl ₂	PtCl ₄	—	—	—	—
II. Natural series ..	—	—	—	MgCrO ₄ ZnCrO ₄	CdCrO ₄	—	—	—
III. Crystallised salts..	—	—	CoI ₂ H ₂ O	—	—	CoI ₂ ,6H ₂ O	—	—
IV. Other compounds—								
a. Isomorphous groups	Al ₂ O ₃	—	Cr ₂ O ₃	Fe ₂ O ₃	—	—	—	—
b. Bodies containing								
organic or other	—	—	—	C ₁₂ H ₉ N ₂ (NH ₂)	C ₁₂ H ₈ N ₂ (NH ₂) ₂	—	C ₁₂ H ₇ N ₂ (NH ₂) ₃	—
radicals.. ..	—	—	—	K ₂ O.CrO ₃	—	K ₂ O.(CrO ₃) ₂	—	—

and m''' their respective molecular weights, then the specific heat of the first of the series is—

$$\frac{a+b+4c}{m'},$$

and the above expression becomes—

$$\frac{(a+b+4c) \times 273 \times m'}{m'} = (a+b+4c)273$$

and so for the rest, substituting m'' and m''' for m' .

Whence it appears that if all these bodies were white at the absolute zero, then to give them their respective colours at the normal temperature equal amounts of heat have been expended on molecular weights of them. Or if we compare equal weights of such a series of bodies, then the greater the change of colour effected through the given range of temperature, and the less the amount of heat expended, *i.e.*, the calories used up in changing equal weights bear an inverse relation to the molecular weights, being with every probability their reciprocals, viz., $\frac{1}{m'}$, $\frac{1}{m''}$, and $\frac{1}{m'''}$.

The idea here introduced of universal whiteness at absolute zero brings us round to the case of white bodies at the normal temperature. At higher temperatures they may change, and if they do one may safely predict that it will be in accordance with the law of colour, *i.e.*, in the race of colour change the bodies of higher molecular weight will get nearer to the black end of the scale than those of lower molecular weight comparable with them. This is illustrated by the oxides of magnesium and zinc, which are both white at normal temperatures, but at a temperature below red heat the ZnO has become yellow and the MgO still remains white by contrast.

In conclusion of this paper I would add a word regarding the law of colour and constitution enunciated in my first communication to meet objections which have been raised against it. The Table above may be taken as types of the comparable bodies which conform to it.

Out of 508 examples of bodies studied the exceptions to the law of colour amount to about 6 per cent, and of these exceptions the largest number come under the third division.

Halifax, Jan. 30, 1893.

THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS.

By GERHARD KRÜSS.

A SOLUTION of the earthy chlorides behaves on electrolysis like the solution of a hydroxide in dilute hydrochloric acid. (Cl)₂ and (H)₂ are evolved at the electrodes, the solution of the earthy chloride loses more hydrochloric acid, and allows hydroxide to deposit in an increasing quantity in proportion to the decrease of the solvent.

In this manner varying quantities of earths can be eliminated from the chloride solutions of mixtures of the rare earths, when it is to be expected that those bases which prove weakest in contact with hydrochloric acid are first thrown down as hydroxides as soon as a part of the hydrochlorides are decomposed by electrolysis. The stronger bases remain still in solution as mere stable

chlorides. In order to withdraw the hydrochloric acid from a chloride solution of rare earths as uniformly as possible in all parts of the liquid, electrodes with large surfaces were applied. (This is requisite to prevent the proportion of hydrochloric acid from becoming unequal in different parts of the liquid, when consequently feeble and strong bases of the series of the rare earths are simultaneously deposited from different parts of the solution). The arrangement of the experiment was as follows:—

The solution of the earthy chloride, as neutral as possible,* containing about 3 grms. of earth in 200 c.c. solution, was put in a beaker of 15 c.m. in diameter. The negative electrode was extended along the internal circumference of the beaker; it consisted of a net of copper wire in the shape of a cylinder jacket, and extended from the bottom of the vessel to the surface of the liquid. As a positive pole there was used the carbon of a Bunsen element placed in the axis of the beaker, and kept from contact with the negative pole by means of glass rods. The current was supplied by four Bunsen elements arranged in series, the zinc pole of one connected with the carbon pole of the following element. The liquid became heated to 40° and in ten minutes 0.4 gm. of the earth were deposited as a heavy, dense precipitate. The appearance of this deposit is quite different from that of the light, bulky matter obtained on precipitating the chloride solutions of the rare earths with ammonia. The first separation obtained by electrolysis was filtered off, the filtrate was then again exposed to the current for ten minutes in the same manner as before, and so a second, third, &c., fraction of hydroxide was separated from the mixture of the earths. In order to show the *modus operandi* of this procedure, we communicate an experiment in which an yttria-earth dissolved as chloride was submitted to electrolysis.

The yttria employed was analysed. From the result of the determination of the equivalent there was calcu-

lated: $R = 97.1$ for the earth in question. It was the second member of a series of fractions in which a large quantity of yttria earth was decomposed by precipitating the chloride with aniline in an alcoholic solution:—

Precipitation 1.	Precipitation 2.	Precipitation 3.
^{III} R = 99.58	^{III} R = 97.7	^{III} R = 102.5

By aniline as well as by ammonia there are thrown down in the first precipitation in general a more feebly basic oxide than in the second, and in the third more powerful bases than in the second precipitation. Constituents both of the first and of the third precipitation† must also be present in the second precipitation according to the general behaviour of the rare earths. On the further elaboration of the latter, according to a method which re-arranges the constituents of this fraction (No. 2), according to their basicity, a similar series of fractions will result from the precipitation No. 2, as it is shown by the above fractions in Fig. 1.

The impure yttria (precipitation No. 2, $R = 97.7$), was

* Neutrality is obtained by evaporation on the water-bath.

† R of fraction 1, as of fraction 3, is in the above case $>R$ than fraction 2.

now submitted to electrolysis as a chloride solution, and resolved into five fractions by the partial separation of hydroxide. For the separation of each of the five precipitates ten minutes were required. After determining the combining weight of the earths the following mean values are calculated for R in the several fractions.

Separations by Electrolysis.				
No. 1.	No. 2.	No. 3.	No. 4.	Residue.
107'39	93'5	105'23	107'7	137'31

This curve quite answers the expectations which might be entertained concerning the decomposition of the material R=97'1 of No. 1. Both branches of the curve to the right and the left ascend more suddenly from the minimum (R=93'5) of No. 1.

Hence, the electrolysis of the solutions of the rare earths seems a suitable method of working up the earths. The examination of this subject is being continued. The above experiments were conducted by the author's assistant, Dr. Karl Hofmann.—*Zeit. für Anorgan. Chemie*, vol. iii.

ON THE REACTIONS OF FERRIC SALTS WITH SULPHOCYANATES.

By H. M. VERNON, B.A.

IN the CHEMICAL NEWS, vol. lxvii., p. 1, Dr. Gladstone makes some criticisms on a paper of mine of the above title, which appeared in the CHEMICAL NEWS, vol. lxvi., p. 177. In the first place, I must apologise for having been so careless as to miss noticing his account of experiments on the effect of adding water to solutions of ferric sulphocyanate, and also for partly misunderstanding the point of view from which his experiments were made. At the same time, I do not understand why, having noticed the effect of water, Dr. Gladstone persisted in his method of colour comparison of the various solutions. In this method one solution was diluted with water till when viewed horizontally in a test-glass it appeared of the same tint as the standard solution, the total volume of the liquid being taken as a measure of the amount of ferric sulphocyanate present in the solution. As the addition of water was known to cause a decrease in colour effect, the amount added surely could not be taken as a measure of the additional ferric sulphocyanate formed, and it is not remarkable that, as Dr. Gladstone himself found, the results obtained were not expressible in the form of an equation.

Dr. Gladstone quite correctly states that my results are never in direct contradiction to his, but he blames me for the very theoretical conclusions I have drawn from them. I do not think, however, that any other conclusions can be drawn from the experiments on the colour values of solutions of potassium sulphocyanate and varying quantities of ferric chloride at various dilutions, than that the effect of adding ferric chloride is twofold, viz., that it causes an increase of colour by rendering the ferric sulphocyanate molecules present more stable and less dissociated, and that it causes a decrease of colour by actually dissolving or in some way decomposing some of these molecules. How else can the colour values calculated for infinite concentration be accounted for? The actual reactions of salts such as ferric chloride and potassium sulphocyanate are unsuitable for directly demonstrating the law of mass, for potash has so very much greater an affinity for hydrochloric acid than for sulphocyanic acid, and also is so very much stronger a base than ferric oxide, that practically, to within 98 per cent or more, there are only present potassium chloride and ferric sulphocyanate in a solution of equivalents of these salts at infinite concentration. This conclusion was of course

impossible to prove experimentally, the experiment with barium sulphocyanate and ferric sulphate merely showing that the removal of the other reacting salt from the solution produced practically no increase of colour.

With regard to the changes of colour on heating ferric sulphocyanate solutions, Dr. Gladstone mentions that he has noticed that ferric chloride solutions themselves greatly increase in colour on heating, and he considers that this has led me astray in my explanation of the results. In the CHEMICAL NEWS, vol. lxvi., p. 141, I myself have given numerical values for the effect of heating moderately concentrated ferric chloride solutions. These results show that the change of colour is considerable, and also that it is greater the more dilute the solutions, as Dr. Gladstone himself found. Only a small part of the change on heating the ferric sulphocyanate solutions is due to the ferric chloride, however, for, as Dr. Gladstone has shown, the addition of one equivalent of potassium sulphocyanate to 100 equivalents of ferric chloride increases the colour effect twentyfold. The results on p. 214 prove that my explanation was correct. Thus, on heating solutions of one equivalent of potassium sulphocyanate and 100 equivalents of ferric chloride, at a dilution of 160 litres, from 20° to 60°, the colour effect increases 41 per cent. On heating a solution containing the same number of equivalents, only diluted to 800 litres, the increase of colour effect at 60° is only 18 per cent. In this solution, therefore, though the ferric chloride must have caused a considerably greater effect than in the more concentrated solution, the increase of colour on heating is less than half. I think, therefore, that it must be concluded that ferric sulphocyanate solutions under suitable conditions increase in colour effect on heating, according to the general rule found to obtain for other salt solutions by Dr. Gladstone (*Phil. Mag.*, 1857) and independently by myself (CHEMICAL NEWS, vol. lxvi., p. 141).

In conclusion, I must thank Dr. Gladstone for criticising my paper in so kindly a spirit. I hope my experiments and remarks may be taken rather as a continuation of his experiments, which at the time they were published had such an important effect on the progress of chemical inquiry, than as a hostile criticism of them.

MANURIAL EXPERIMENTS WITH TURNIPS.*

By C. M. AIKMAN, M.A., B.Sc., F.R.S.E.,
Lecturer on Agricultural Chemistry, Glasgow and West of
Scotland Technical College, and Glasgow University
Extension Board.

(Continued from p. 59).

THE turnips were lifted in the beginning of December, and weighed as follows:—

No.	Manure.	Produce.		Increase over nothing plots.	
		T. cwt.	qr.	T. cwt.	qr.
1.	Nothing	3	8 3	—	—
2.	4 cwt. super	19	0 0	10	17 3
3.	8 cwt. super	19	15 0	11	12 3
4.	6 cwt. slag	17	1 1	8	19 0
5.	12 cwt. slag	17	16 1	9	14 0
6.	Nothing	12	15 3	—	—
7.	6 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda ..	28	0 0	19	17 3
8.	6 cwt. slag and 15 tons dung	24	12 2	16	10 1
9.	12 cwt. slag and 15 tons dung	25	18 3	17	16 2
10.	12 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda ..	28	2 2	20	0 1

No. 11 was not weighed, as Mr. Graham considered it valueless as a nothing plot, as it received slag blown over from No. 10.

* From the Transactions of the Highland and Agricultural Society of Scotland.

In calculating the nothing plots I have taken the mean of plots Nos. 1 and 6. Plot 6 received a little slag from No. 5; and that, Mr. Graham thinks, will account for the difference. With regard to No. 1, I wrote Mr. Graham on receiving his results, asking him if he was quite convinced of their accuracy, and received the following reply: "The statement I have given in regard to No. 1 (nothing plot) is thoroughly correct. There was no circumstance connected with it in any way calculated in the least to give it an unfair chance. Every plant lived on till the time for storing, but they were useless dwarfs."

It will be seen from the above results that the plots which show the biggest returns are Nos. 7 and 10—those which received slag, dung, and nitrate of soda. There is very little difference between the two. Nos. 8 and 9 come next—those which received slag and dung; No. 9, which received the larger quantity of slag, giving about 1½ tons more turnips than No. 8. Between plots Nos. 2 and 3—viz., those which received "super" alone in greater and smaller quantity respectively—there is not much difference, only some 15 cwt., not sufficient to justify the additional expense of the larger quantity of super.

The plots which show the lowest returns are those which received slag alone. Whether, however, this shows slag to be inferior in worth as a manure in this case to super cannot be inferred until we compare the cost of the manures. This, accordingly, will be seen from the following table:—

No.	Manure.	Cost.	Value of increase in crop.
2.	4 cwt. super.. ..	£0 11 0	£4 6 0
3.	8 cwt. super.. ..	1 2 0	4 13 0
4.	6 cwt. slag	0 6 0	3 11 6
5.	12 cwt. slag	0 12 0	3 17 6
7.	6 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda ..	5 6 0	7 19 0
8.	6 cwt. slag and 15 tons dung	4 16 0	6 12 0
9.	12 cwt. slag and 15 tons dung	5 2 0	7 2 8
10.	12 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda ..	5 12 0	8 0 0

(N.B. The turnips were sold at 8s. per ton).

An examination of the above table will show that in every case there is a fair margin of profit, the most profitable being Nos. 2, 3, 4, and 5, those which received mineral manure alone. Of these No. 2 shows best—that which received 4 cwt. super per acre—a profit of £3 15s. No. 3 comes next, showing a profit of £3 11s.; while Nos. 4 and 5 are exactly the same. In this case, then, it may be said that the slag is weight for weight one half as valuable as the super. As, however, the slag contains only a little more than half the percentage of phosphates, the unitary value of the phosphates in each is practically the same.

In these experiments, as in the previous series, the dung does not justify its application. By comparing the results of plots Nos. 4 and 8 it will be seen that the addition of 15 tons of farmyard manure, costing £4 10s., only gave an increase of 7½ tons, possessing the value of £3, while comparison between Nos. 5 and 10 will show a similar result.

Comparing plots Nos. 7 and 8, and 9 and 10, it will be found that, in the first case, 1 cwt. of nitrate of soda, costing 10s., was the means of increasing the crop to the extent of over 3 tons, value £1 7s.; while in the second, the increase amounted to only about 2 tons, value 17s.—sufficient, however, to show a profit.

The next series of experiments about to be described were those carried out by Mr. A. Stevenson, at his farm of Parkhill, Tarbolton, Ayrshire. The soil of the field experimented upon was a sandy loam, naturally not fertile, but which had been liberally treated for many years,

and yielded fair crops. The mechanical and chemical analysis of the soil is as follows:—

(a) Mechanical analysis—

Clay	52.41 per cent
Sand	47.59 "
	100.00

(b) Chemical analysis (soil dried at 212° F.)—

Organic matter (containing nitrogen, 0.207)	7.770
Iron sesquioxide and alumina ..	3.900
Lime	0.616
Magnesia	0.200
Potash	0.173
Soda	0.154
Sulphuric acid	0.073
Phosphoric acid	0.207
Insoluble siliceous matter, chlorine, carbonic acid, &c.	86.907
	100.000

Mr. Stevenson describes its past history as follows:—"In 1883 the field was ploughed out of lea, and a crop of oats taken. The oats received 1½ cwt. super, 1 cwt. dissolved bones, and 1 cwt. nitrate of soda per acre. In 1884 there was a crop of potatoes, which were manured with 18 tons farmyard manure, 2 cwt. super, 2 cwt. dissolved bones, and 1 cwt. sulphate of ammonia per acre. In 1886 there was a crop of hay, which was manured with 1 cwt. super, 1 cwt. dissolved bones, and ½ cwt. sulphate of ammonia per acre. In 1887 a crop of hay was grown, which received the same quantity of manure as was applied the previous year; and in 1888 a crop of oats was grown, which received the same manures as those applied in 1883."

The ground is low-lying, and has a southern as well as a northern exposure. The plots were ten in number, each being 1 roth of an acre in extent.

The following is a statement of the different plots, with the quantities of manures each received and the produce yielded:—

No.	Manure.	Produce. Tons. cwt.	Increase over nothing plots. Tons. cwt.
1.	Nothing	16 12	— —
2.	6 cwt. slag	19 0	2 8
3.	4 cwt. super	20 17	4 5
4.	12 cwt. slag	23 12	7 0
5.	8 cwt. super	23 0	6 8
6.	12 cwt. slag and 20 tons dung	28 7	11 15
7.	12 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda	31 0	14 8
8.	6 cwt. slag and 20 tons dung	26 15	9 3
9.	6 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda	30 10	13 18
10.	5 cwt. super and 20 tons dung	33 0	16 8

The largest returns are obtained from plot No. 10—that receiving 5 cwt. super and 20 tons dung—viz., 33 tons per acre, or 16 tons 8 cwt. of an increase over the average of the nothing plots.

The following table shows the value of the manures and the value of the increase of crop produced by them. The most profitable plot, it will be seen, is No. 4, which received slag alone at the rate of 12 cwt. per acre. Again it will be seen that, with the exception of plot No. 10, farmyard manure applied did not give its value in increase of crop.

No.	Manure.	Cost.	Value of increase in crop.
2.	6 cwt. slag	£0 6 0	£1 9 0
3.	4 cwt. super.. ..	0 11 0	2 11 0
4.	12 cwt. slag.. ..	0 12 0	4 4 0
5.	8 cwt. super.. ..	1 2 0	3 17 0
6.	12 cwt. slag and 20 tons dung.	6 12 0	7 1 0
7.	12 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda ..	7 2 0	8 13 0
8.	6 cwt. slag and 20 tons dung.	6 6 0	5 10 0
9.	6 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda ..	6 16 0	8 1 0
10.	5 cwt. super and 20 tons dung.	6 13 9	9 17 0

A comparison of plots Nos. 2 and 3, and Nos. 4 and 5, will show that in the first case super shows better than the slag, while in the second case slag shows better than the super. Again, in both cases where the nitrate of soda has been used it shows a very marked increase. Thus in plot No. 7, 1 cwt. of nitrate of soda (costing 10s.) has given an increase of crop over plot No. 6 of the value of £1 12s., while in plot No. 9 the increase over plot No. 8 is £2 11s.

(To be continued).

ON THE GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 56).

Dumas's Research Critically Considered.

DUMAS's method, or rather that of Berzelius (because it was he who invented it, as every student of chemistry is aware), consists in this, that a given quantity of oxide of copper is reduced in hydrogen gas, and the loss of weight suffered, that is to say, the oxygen given up by the oxide compared with the weight of water produced. This is no occasion for describing the exact *modus operandi* which was adopted by Berzelius, but we must name the refinements upon it which were introduced by Dumas. One of these was that he worked on a far larger scale than his predecessor had done, and another, that he took care to purify and dry his hydrogen more fully by passing it through long successive columns of (1) solution of nitrate of lead, (2) solution of nitrate of silver, and (3) pumice soaked in oil of vitriol or powdered over with phosphoric anhydride. Dumas, besides, took special care to not allow the surplus hydrogen and the air which he passed through the water receptacle at the end of an experiment to escape without having first been most thoroughly dehydrated by means of tared tubes containing one or the other of the two dehydrators named.

But the principal improvement by Dumas was that he evacuated his reduction tube, both before and after the experiment, before taking it to the balance. The difference of the two weighings thus gave the *true* weight of the oxygen quite directly, and the errors, which would otherwise have been caused by the gases condensed in the pores of the oxide and of the metal, were eliminated at the same stroke. The water produced was weighed in the ordinary way—we mean “not in *vacuo*.” Referring to Dumas's memoir for more detailed information on his mode of working, we will now pass to a review of his results, as tabulated by him on page 200 of his memoir. A superficial examination of this table sufficed to show

that it is not free from misprints. To detect these we recalculated all his “*equivalents bruts*,” and in doing so had no difficulty in spotting and rectifying the errors. The results of our calculations are included in the following Table:—

Number.	<i>n</i> .	<i>k</i> .	<i>k</i> — <i>k</i> ₀ .	Order of residuals.
3 ..	20	1'12481	—0'00066	19
19 ..	31	1'12488	—0'00059	18
2 ..	20	1'12490	—0'00057	17
8 ..	46	1'12500	—0'00047	16
10 ..	52	1'12504	—0'00043	15
1 ..	13	1'12505	—0'00042	14
4 ..	57	2'12506	—0'00041	13
16 ..	37	1'12506	—0'00041	12
11 ..	52	1'12512	—0'00035	10
12 ..	60	1'12533	—0'00014	3
7 ..	35	1'12546	—0'00001	1
15 ..	56	1'12558	+0'00011	2
5 ..	76	1'12566	+0'00019	4
6 ..	44	1'12568	+0'00021	5
17 ..	34	1'12575	+0'00028	6
13 ..	62	1'12577	+0'00030	7
18 ..	32	1'12580	+0'00033	8
14 ..	52	1'12581	+0'00034	9
9 ..	60	1'12585	+0'00041	11

Column 1 gives the order in which the several experiments are enumerated on Dumas's table; col. 2, under “*n*,” the weights of oxygen operated upon, rounded off to the nearest integer number of grms.; col. 3, for each experiment, the weight of water obtained per grm. of oxygen, as “*k*.” In the heading to col. 4 the symbol *k*₀ stands for the most probable value of the ratio H₂O : O calculated by us; the numbers in col. 5 arrange the values *k*—*k*₀ in the order of their magnitude, irrespective of their signs.

For any one of the nineteen syntheses we have an equation of the form $W - Sk_0 = \delta$, where *S* stands for the (exact) weight of oxygen and *W* for the weight of water found, and δ for the error in the water-weight found, supposing *k*₀ to be the true value of H₂O : O. We brought the equation into the form $S(k - k_0) = \delta$ (which was more convenient to us, because we had already calculated the values *k*), and then, substituting for every *S* its corresponding *n*, calculated that value for *k*₀, which, supposing it to be substituted in all the equations, would reduce the sum of the squares of the values δ to its minimum. The result was *k*₀ = 1'12547. From the list of errors in the last column we calculate that the “probable” error of a single determination is $r = \pm 0'000303$, which, indeed, is not far removed from the tenth of the values *k*—*k*₀; for the probable error of the mean we find $r_0 = \pm 0'000070$. In all that we have stated the word “error,” of course, means that part of the total error which is owing to accidental causes, and even in this sense *r*₀ does not represent more than a fraction of the uncertainty. For a guess the latter may be put down at three times the probable error; if we do so our calculation shows that, supposing Dumas's determinations were free of method errors, the true value of *k* could be said to lie between 2'1253 and 1'1257.

In the present case the accidental part of the error of any one result may be taken as being a function of the errors of the four weighings involved. Assuming, for an approximation, that the probable values of these four errors were all of the same magnitude $\pm x$, we have for the probable error in the water-weight, \bar{W} , and for that in the oxygen-weight, *S*, the same value, $x\sqrt{2}$, and for the relative probable errors in *W*, and in *S* or $\frac{1}{S}$, the expressions $\frac{x\sqrt{2}}{\bar{W}_0}$ and $\frac{x\sqrt{2}}{S_0}$, respectively. Hence we may write—

$$W \times \frac{1}{S} = \left(\bar{W}_0 \pm \frac{x\sqrt{2}}{\bar{W}_0} \bar{W}_0 \right) \times \left(\frac{1}{S_0} \pm \frac{x\sqrt{2}}{S_0} \cdot \frac{1}{S_0} \right)$$

* *Proceedings of the Philosophical Society of Glasgow.*

Hence, according to a rule of the method of the last squares, if r be the probable error of the product,

$$r^2 = \frac{W_0^2}{S_0^2} \cdot \frac{2x^2}{S_0^2} + \frac{1}{S_0^2} \cdot 2x^2.$$

Hence, as $\frac{W}{S} = 1.125$ very nearly,

$$r = \pm 2.129 \frac{x}{S_0}.$$

Dumas's average value for S was about 44 grms.; hence we have for what one might call his average "experiment,"—

$$x = \pm 6.2 \text{ m.grms.}$$

In other words, the value 0.0003 recorded above for the probable error of a single experiment may be explained by assuming that the probable error of each of his four weighings was ± 6 m.grm., and that the real error varied from something like -18 to something like $+18$ m.grm.; and this is a fair enough guess, considering that the apparatus he used were uncommonly heavy and bulky. His reduction tube, for instance, cannot have displaced much less than 600 m.grms. of air, and supposing the density of the air to have changed between the two weighings by $1/30$ of its value, this alone would make his oxygen-weight wrong by ± 20 m.grms. To pass to "Dumas's Method Errors," the most obvious of these is the one caused by the unavoidable presence of atmospheric air in even the most carefully prepared hydrogen gas. As already stated in the prefatory note, Dumas sought to eliminate this error by calculating for each of his syntheses the weight of water produced from the atmospheric oxygen introduced as part of the sulphuric acid used for the making of the hydrogen, and deducting the result from the total weight of water as found by direct weighing. His mean "*equivalent corrigé*" is by 0.00018 less than his corrected mean. Deducting this from our $k = 1.12547$, we have for the corrected number 1.12529, or, for $O = 16$, $H = 1.00232$. Unfortunately, however, Dumas does not tell us how he procured the data for his correction; and, besides, if we consider that his hydrogen had to travel through some seven metres of U-tubes, charged, some of them, with porous materials, before it reached its destination, it is impossible not to suspect that his gas contained other adventitious oxygen, besides that derived from the dilute sulphuric acid which went into the gas-evolution bottle. Under these circumstances we thought we had better try and determine Dumas's adventitious oxygen as far as now possible ourselves, and we thus came to carry out the experiment referred to in the prefatory note as having given us the conviction that his correction was below the truth. This experiment (detailed hereafter as Exp. I.) was, of course, meant to be repeated, and it really was, but only after the intervention of a deal of other work. At the time it struck us that being, unlike Dumas, in possession of a method for the production of a current of absolutely oxygen-free hydrogen, the best thing we could do was to effect a series of quantitative syntheses of water by means of such gas, provided only we took care to maintain our critical attitude, and to do to our own work what we had originally proposed to do in reference to that of our great predecessor. As an important preliminary, we tried to ascertain whether it is possible to pass a current of hydrogen over a surface of red-hot glass without producing at least traces of water from it and the oxygen of the bases in the outer skin of the tube.

For this purpose we carried out two series of experiments. In the first we passed the gas over relatively large surfaces of red-hot glass, and weighed the water produced from a known volume of hydrogen. In the second experiment we aimed more directly at the probable magnitude of supposed error by carrying out a number of quantitative syntheses of water with, in general, large known volumes of hydrogen, but varying

weights of oxide of copper. Supposing S to stand for the weight of oxygen used up in a given synthesis, W for the weight of water produced, and V for the number of litres of hydrogen which passed through the hot reduction tube over and above the minimum which would have sufficed to convert those S grms. of oxygen into water, we have $W = kS + k'V$, and theoretically all that is required for the determination of the constants are two syntheses—one carried out with little, and the other with a large excess of hydrogen gas. But in practice it is better to determine the first constant k (which obviously, if we weigh in air, is not the true value of $H_2O : O$) by means of a few experiments with relatively large quantities of oxide of copper and small excesses of hydrogen, and then to substitute this k in the calculation of syntheses made with small quantities of the oxide to find k' . We, however, commenced with these latter determinations, and, in their original interpretation, assumed that k was equal to 1.125 exactly, which in a practical sense was confirmed by the syntheses subsequently carried out with large weights of oxide of copper. These syntheses were quite completed and calculated when we made a very unwelcome discovery. To prepare for the (it does not matter now what) experiment, we had filled a Dumas system of hydrogen purifiers with the gas by means of a Kipp, closed the outlet, and left the apparatus in this condition over night. When we turned on the hydrogen on the following morning, the gas was found to smell so strongly of sulphurous acid that it would have been impossible not to notice it. We had made quite sure of the absence of this impurity from our vitrioled pumice; hence it was clear that it had been produced from the sulphuric acid by its prolonged contact with hydrogen. But Dumas's syntheses, as we are informed, always took some ten hours for their execution; hence his hydrogen must have been contaminated with sulphurous acid in all those cases at least in which he dehydrated it by means of oil of vitriol. We accordingly instituted a comparison of the results of these experiment with those which he arrived at when he dehydrated his gas with phosphoric anhydride, but we could not see any marked difference, and concluded that he used the more powerful dehydrator, not by itself, but as an auxiliary to oil of vitriol. But, be this as it may, our own syntheses, although they were carried through in far less time, and although our vitrioled pumice tubes were far smaller than Dumas's, must in some measure have been effected by the same error. It was also clear that what had so far been put down by us as "adventitious oxygen O_2 ," had partly consisted of SO_2 . We therefore made a series of critical experiments to determine the magnitude of the corresponding error, and, in our final series of syntheses, used fused caustic potash combined with phosphoric anhydride as sole dehydrators. After this digression we will now proceed to give a brief but sufficiently detailed account of all those of our experiments which bear more directly on the question under discussion.

I.—Determination of the Adventitious Oxygen in Dumas's Hydrogen.

Experiment I.—The apparatus used consisted of the following successive parts:—

1. A "Kipp," or a combination of two Kipps (*vide infra*), charged with ordinary (we mean unboiled) dilute sulphuric acid.

2. A close imitation of Dumas's set of purifying tubes for the hydrogen, namely:—

(a) A tube charged with glass fragments and a strong solution of nitrate of lead.

(b) A similar tube with solution of sulphate of silver. In these two tubes the volume of reagent was so adjusted that the gas had to bubble through a not inconsiderable column of liquid in the bent portion.

(c) A third tube, of which the entrance limb was charged with fragments of pumice which had

been boiled with solution of caustic potash, and the other with fragments of the fused reagent.

(*d* and *e*) Two tubes charged with fragments of fused caustic potash.

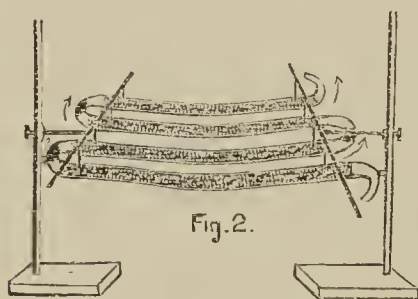
(*f* and *f'*) Two tubes charged with fragments of pumice soaked in oil of vitriol.*

The only deviation from Dumas's design which we allowed ourselves consisted in this, that not having such very large U-tubes as he used at hand, we gave our tubes the form of rather flat V's, as shown by Fig. 2.

Our tubes, however, had the same length as Dumas's, so that the gas, as in his case, had to travel through about seven metres of purifying tubes on its journey.

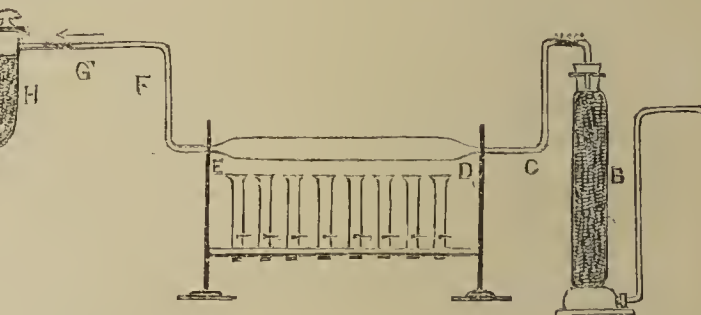
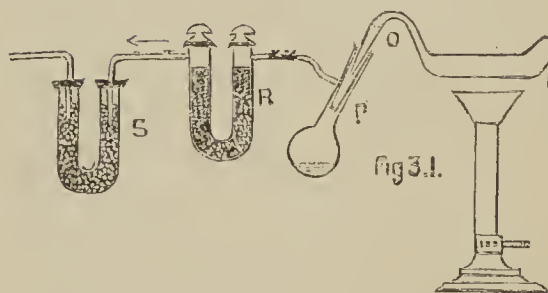
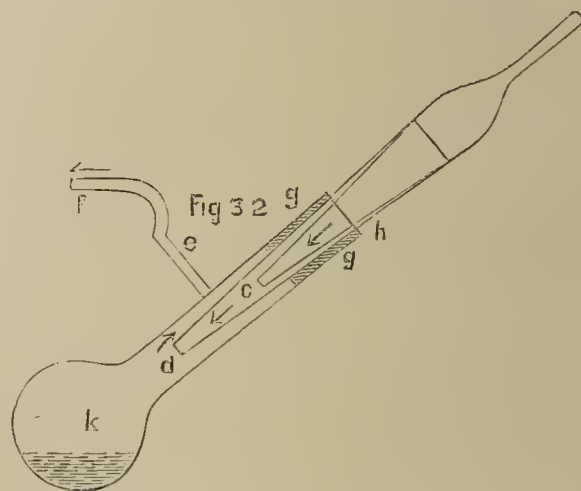
3. A tared "witness tube," G, charged with vitrioled pumice.

4. A combustion tube, 370 m.m. long, and 15 m.m. wide inside, charged with as thick a closely wound spiral of fine copper gauze as it would hold, and then drawn out at both ends to avoid the use of corks or indiarubber stoppers.



In the actual experiment, the first step was to pass hydrogen through the Dumas purifiers until the gas would have been deemed free of air for any ordinary purpose. The weighed witness tube, G, and the copper-gauze tube were then attached, and after the copper had become red hot, three further litres of hydrogen were sent through the apparatus to purge the copper from its water and oxygen. This being done, the weighed tube, K, and its protection tube were attached, and the experiment continued until a sufficiency of hydrogen had accumulated in the Pisani. At the end, the tubes K and L were detached, the hydrogen in the former displaced by vitriol-dried air, and this tube weighed—the flames under the copper gauze tube being turned off immediately after the removal of K. As soon as the copper tube had cooled down sufficiently, the witness tube, G, was detached and got ready for the balance. The volume of hydrogen operated upon amounted to 12 litres, which passed through in 3.5 hours. Tube G gained 0.2 m.grm.; tube K, 3.45 m.grm., or 0.288 m.grm. per litre of hydrogen used.

Experiment II.—(Done long after I.). The apparatus used differed from that used in I. only in this, that in



5 and 6. Two U-tubes charged with vitrioled pumice; the first, K, was tared; the second, L, not; because it served only as a protection tube against ingress of vapour of water from the atmosphere, or from No. 7, which was a large graduated "Pisani bottle," in which the outgoing gas was collected and measured.

The following shows the sequence of the apparatus:—

Kipp.	Dumas's purifiers.	U-tube. vitriol.	Combustion tube.	U-tube vitriol.	U-tube vitriol.	Pisani.
(1)	<i>a, b, c, d, e, f, f'</i>	G	Red hot copper.	K	L	(7)

* We will avail ourselves of this opportunity for stating how we prepared our vitrioled-pumice tubes. After having made sure of the absence of nitrogen oxides and of sulphurous acid from our vitriol, a quantity of cut-up pumice was placed in a large platinum basin, covered with a large excess of the acid, and the acid then kept at a boiling heat until about one-half of it had volatilised. The whole was then allowed to cool under a bell-jar, the surplus vitriol poured off, and the "vitrioled pumice" at once transferred to its U-tubes. When a tube had to be re-charged, it was filled completely with fresh acid (previously boiled down in a platinum basin to expel more volatile impurities), allowed to stand for ten minutes, and the surplus vitriol then poured off. This washing process was repeated once, and the tube then deemed ready for use.

place of the copper-gauze tube we inserted the reduction tube of our apparatus for the quantitative syntheses (L O in Fig. 3) full of reduced copper as it came from one of these. The volume of hydrogen operated upon was ten litres, and the weight of water produced from it = 7.65 m.grm., but the witness tube corresponding to G of Exp. I. gained 10.8 m.grm.

Experiment III.—(Done immediately after II.). In this experiment we obtained 8.2 m.grm. of water from 11 litres of hydrogen, or 0.745 m.grm. per litre. The witness tube this time gained only 0.4 m.grm.

Experiment IV.—(Done long after the preceding ones, and after we had come to observe the reducing action of hydrogen on oil of vitriol). The apparatus consisted of the following successive parts:—

1. A Kipp.
2. The set of Dumas purifiers up to the last caustic potash tube, designated as "(2) d" under Experiment I. The two vitriol tubes, *f* and *f'*, were omitted.

3. From *d* the gas passed on successively to a tared witness U-tube, *K*, charged with recently fused caustic potash, and followed by a tared U-tube, *P*, containing pumice and phosphoric anhydride, respectively (*vide infra*, under "final syntheses"); the reduction tube full of reduced metallic copper; a tared U-tube, *K*₁, and a witness U-tube, *P*₁, charged with fused caustic potash and phosphoric anhydride, respectively; a protection tube containing fused caustic potash; and, lastly, the graduated Pisani bottle.

The exact *modus operandi* needs not be described; it suffices to state the results as follows:—The volume of hydrogen operated upon was 12 litres; the tubes *K* and *P* gained 1.5 and 0.2 m.grm. respectively, the tubes, *K*₁ and *P*₁, 2.5 m.grm. and *nil*. Hence, water produced 2.5 m.grm. or 0.208 per litre of hydrogen used.

Experiment V.—(Followed immediately after No. 4, and was done in exactly the same manner). Increase of weight suffered by tubes *K*, *P*, *K*₁, *P*₁, = 0.7, 0.2, 2.3, 0.2 m.grm. respectively; volume of hydrogen used = 12 litres; hence, water produced per litre of hydrogen = $2.5 : 12 = 0.208$.

Hence we had, for the potential water in Dumas's hydrogen, m.grms. per litre:—

	Experiment—				
	I.	II.	III.	IV.	V.
From O ₂ and SO ₂ ..	0.288	0.765	0.745		
From O ₂ alone ..				0.208	0.208

In the case of Nos. II. and III. the gas probably was largely contaminated with sulphurous acid.

(To be continued).

THE INSTITUTE OF CHEMISTRY.

THE following letter, addressed by Prof. Thorpe to the President of the Institute of Chemistry, has been forwarded to us for publication:—

Royal College of Science,
South Kensington, S.W., Feb. 3, 1893.

DEAR MR. PRESIDENT,

The action of the Council of the Institute of Chemistry with respect to the Chemical Society, in their decision at the last meeting, is, in my judgment, so significant of what may now be considered the official relations of the Institute towards the sister Society, that I am compelled to tender my resignation as a member of the Council, and at the same time to withdraw from the Institute.

The mover of the resolution to omit the letters F.C.S. from the Register of the Institute, based his argument ostensibly on the assumption that Fellowship of the Chemical Society is not to be regarded as a "professional qualification." Although this resolution was subsequently amended as follows: "That in future all letters indicating membership of any society, except the Royal Society (London), be omitted in the Register from all names of members of the Institute," it will be obvious to anyone who turns to the present Register that the amended resolution, which was adopted by the Council, is practically directed against the Fellows of the Chemical Society.

The Council must know that it has no power to compel any of the members of the Chemical Society to omit the letters F.C.S. after their names if they are minded to use them: not even if the use of such letters should be construed as a "breach of decorum" in the revised code of professional ethics which the Council is about to elaborate.

It is, I am informed, very questionable whether, if a Fellow of the Institute, who is at the same time a Fellow of the Chemical Society, required that he should

be designated in your Register as a Fellow of the Chemical Society by the letters F.C.S., which by use and wont are understood to indicate such Fellowship, the Council could prevent it.

There is no greater inherent value or property in the letters F.I.C. than in those of F.C.S. Whatever value may be associated with those letters is a matter of individual appraisal, depending upon the estimation by the valuer of the worth and dignity of the particular Society.

I am, of course, ready to admit that the majority of the present Council of the Institute are not actuated by unfriendly feelings towards a Society which they recognise has for more than half a century, by its publications, its research fund, and its library, fostered to the best of its power the study of Chemical Science in this kingdom; what I regret is that in following the initiative of a section which has hitherto shown itself more ready to interfere in the proceedings of the Chemical Society than to contribute to its transactions, they should have put themselves officially in an attitude of antagonism to the Chemical Society, and by seeking to interfere with the individual freedom of their members in a matter which not even the code of professional ethics could rightly take cognisance of, they should have assumed a position from which they might be compelled to retreat.

Yours very truly,
Prof. Tilden, D.Sc., F.R.S. T. E. THORPE.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, January 27th, 1893.

WALTER BAILY, M.A., Vice-President, in the Chair.

MR. T. W. MORTON was elected a member of the Society.

Prof. S. P. THOMPSON, F.R.S., made a communication on "*Japanese Magic Mirrors*," and exhibited numerous specimens showing the magic properties. Referring to the theory of the subject, he said the one now generally accepted was that proved by Professors Ayrton and Perry in 1878, who showed that the patterns seen on the screen were due to differences in curvature of the surface. The experiments he now brought forward fully confirmed their views.

Brewster had maintained that the effects were due to differences of texture in the surfaces causing differences in absorption or polarisation, but the fact that the character of the reflected image depended on the convergence or divergence of the light and on the position of the screen, showed this view to be untenable. Another proof of the differing curvature theory was then given by covering a Japanese mirror with a card having a small hole in it. On moving the card about, the disc of light reflected from the exposed portion varied in size, showing that the curvatures of portions of the surfaces were not the same. The same fact was proved by a small spherometer, and also by reflecting the light passing through a coarse grating from the mirror, the lines being shown distorted. To put the matter to a test demanded by Brewster, he had a cast taken from a mirror by his assistant, Mr. Rousseau; this had been metallised, silvered, and polished, and now gave unmistakable evidence of the pattern reflected from the original.

The true explanation of how the inequalities of curvature were brought about during manufacture had also been given by Professors Ayrton and Perry, but there were some questions of detail on which difference of opinion might exist.

The late Prof. Govi had noticed that warming a mirror altered its possibilities. A thick mirror which gave no

pattern whilst cold, but developed one on being heated, was shown to the meeting.

Professor THOMPSON also showed that a glass mirror having a pattern cut on the back developed magic properties when the mirror was bent. When made convex the reflected pattern was dark on a light ground, and when made concave light on a dark ground. Warming ordinary mirror glass by a heater whose surface was cut to a pattern gave similar effects. Very thick glasses could be affected in this way. On passing a spirit-lamp behind a strip of mirror, a dark band could be caused to pass along the screen illuminated by light reflected from the mirror. By writing on lead foil and pressing the foil against a glass mirror by a heater, the writing was caused to appear on the screen.

Prof. THOMPSON had also found that Japanese mirrors which are not magic when imported could be made so by bending them mechanically so as to make them more convex. In conclusion he showed a large mirror 15" x 11", the reflection from which showed the prominent parts of the pattern on its back, with the exception of two conspicuous knobs; these knobs gave no indication of their existence.

Prof. AYRTON said the simple mechanical production of the magic property described by Prof. Thompson led him to think that some experiments on "seeing by electricity" by the aid of selenium cells, which Prof. Perry and himself made some years ago, might lead to some result if repeated with thinner reflectors. Speaking of the effect of scratching the back of a Japanese mirror, he pointed out that if metal be removed by pressure a bright image was seen, whilst if removed chemically a dark image resulted. Since the original paper on the subject was written, he had been led to modify his views as to the effect of amalgamation, for some time ago he showed the Society how brass bars were bent if one edge be amalgamated, thus proving that enormous forces were developed. He now regarded amalgamation as an important part of the manufacture.

Mr. TROTTER enquired if it had been proved that there was no difference in the metal in the thick and thin parts? One would expect the thin parts to be harder and polished away less.

After some remarks by Mr. J. W. Kearton and Major Rawson, Prof. THOMPSON said the magic effects produced by heating the back of a glass mirror remained for a short time after the heater was removed. The question of whether differences in hardness of the thick and thin parts of a mirror were of consequence in the production of the magic property had been tested by using sheets of brass thickened by pieces soldered to the back as mirrors, and found to be unimportant.

Prof. AYRTON also described an experiment pointing to the same conclusion.

Mr. W. F. STANLEY read a paper on "*The Functions of the Retina. I. The Perception of Colour.*" Referring to Young's three-nerve theory of colour sensation, the author said Prof. Rutherford had pointed out that there was no necessity to assume that different nerves conveyed different colour sensations, for as a telephone wire would transmit almost an infinite variety of sound vibrations, so the nerves of the retina were probably equally capable of conveying all kinds of light vibrations. Prof. Rutherford had further pointed out that the image of a star could not possibly cover three-nerve terminals at once, and therefore could not be seen as white if Young's theory was correct.

The author then described Helmholtz's experiments with a small hole in a screen illuminated by spectrum colours. For red illumination the greatest distance at which the hole could be seen sharply defined was eight feet, and for violet one and a half feet. When the hole was covered with purple glass, or with red and violet glasses superposed, and a bright light placed behind, the eye,

when accommodated for red light, saw a red spot with a violet halo round it, and when focussed for violet light, saw a violet spot with circle of red. These experiments, the author thinks, show that the chromatic sense in distinct vision under critical conditions (*i.e.*, where a single nerve or a small group of nerves is concerned) depends on the colours being brought to foci at different distances behind the crystalline lens. He also infers that the same focal position in the eye cannot convey simultaneously the compound impression of widely separated colours. Helmholtz's observations are further examined in the paper, and a series of zoetrope and colour disc experiments described, which tend to show that the eye cannot follow rapid changes of colour. Changes from red to violet could be followed much more quickly than from violet to red. The red impressions were, however, more permanent. The observed effects were found to depend on the intensity of the light, and also on the distance of the eye from the coloured surface.

Summing up his observations, the author infers that by systems of accommodation of the eye the colours of the spectrum are brought to focus on special parts or points of the rods or cones of the retina, such focal points being equivalent, by equal depths or distances from the crystalline lens, to a focal plane formed across the whole series of nerve terminals. That all the rays of light from one object, or part of an object, of very small area and of any spectrum colour will converge to a point upon a nerve terminal, and that this terminal will be most excited by the light.

At the end of the paper Dr. Stanley Hall's views on nerve structure are examined.

Captain ABNEY thought the results of the zoetrope experiments were what one would have expected when pigmentary colours were used. To be conclusive, such experiments must be conducted with pure spectrum colours. The statement about the size of star images being less than that of a nerve terminal would probably need revision. Speaking of colour vision he said the modern view was to regard light as producing chemical action in the retina, which action gave rise to the sensation of colour. On the author's theory he could not see how colour blindness could be explained.

Mr. TROTTER said he understood Helmholtz to have proved that nerves could distinguish quantity, but not the quality of a stimulus. Since the speed at which stimulus travelled to the brain was about 30 metres a second, the wave length of a light vibration if transmitted in this way would be very small. Taking Lord Kelvin's estimate of the minimum size of molecules of matter, it followed that there must be many wave lengths in the length of a single molecule. This, he thought, hardly seemed possible.

Mr. LOVIBOND pointed out that the observations referred to by the author could be equally well explained on the supposition that six colour sensations existed. The confusion of colours he had mentioned arose from lack of light.

Mr. STANLEY replied to some of the points raised by Capt. Abney.

In proposing a vote of thanks to Mr. Stanley the CHAIRMAN said it had been shown that light could be resolved into three sensations, but it was not known how this resolution occurred.

Prof. S. P. THOMPSON said the gist of Mr. Stanley's paper seemed to be that lights of different colours were concentrated at points situated at different depths in the retina, the violet falling on the part nearest the crystalline lens and the red furthest away. Another view of the action was that the different sensations might be due to the vibrations of longer wave length having to travel greater distances along the nerve terminal before they were completely absorbed.

ROYAL INSTITUTION OF GREAT BRITAIN.
General Monthly Meeting, Monday, February 6, 1893.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—Messrs. Frederick Canton, M.R.C.S., and William Rolle Malcolm.

The Special Thanks of the Members were returned for the following Donations for carrying on investigations on Liquid Oxygen:—Mrs. Bloomfield Moore, £10; Mr. Robert Wilson, £50; Mr. John Bell Sedgwick, £50.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 4, January 23, 1893.

Contribution to the Study of the Function of Camphoric Acid.—A. Haller.—The author shows that direct experiments have confirmed the views which he expressed in *Comptes Rendus*, vol. cxiv., p. 1326.

The Pepto-Saccharifying Power of Blood and of the Organs.—R. Lépine.—The author considers it probable that the production of sugar in blood in presence of water is preceded by the formation of peptone.

The Atomic Weight of Palladium.—A. Joly and E. Leidié.—The mean result of the authors' determinations is 105.438. They purpose re-determining the atomic weights of the metals of the platinum group.

Action of Alkaline Alcoholates upon Camphoric Anhydride and Certain other Anhydrides.—P. Cazeneuve.—The ethers of camphoric acid are less easily saponifiable than those of the succinic and phthalic acids. Its anhydride differs from a lactide or a coumarine.

Zeitschrift für Analytische Chemie.
Vol. xxxii., Part 1.

Critical Studies on the Methods of Determining Sulphur in Sulphides.—Leo P. Marchlewski.—This treatise is too bulky for insertion.

A Rapid Method for the Complete Precipitation of Arsenic as Pentasulphide, and for its Separation from Bismuth, Lead, Antimony, and Analogous Metals.—Fred Neher.—This paper, according to a footnote, has been translated from an English source. But as it is not stated in what English journal it has appeared it will be inserted in full.

Determination of Nitrogen in Nitro-Cellulose.—Edward von Keussler.—This paper requires the accompanying figure.

Sodium Thiosulphate and Potassium and Potassium Permanganate.—C. Luckow.—If different quantities of a solution of sodium thiosulphate of known strength are mixed with so much of a solution of permanganate of known strength, that after acidulating the mixture with dilute sulphuric or nitric acid, or after the addition of a solution of potassium or sodium hydroxide, and after boiling the mixture, permanganate or the higher oxides of manganese are still present in solution and in the acid or acidified alkaline solution the excess of permanganate

is titrated back with a solution of oxalic acid of equal value, we obtain for equal quantities of sodium thiosulphate equal quantities of the solution of permanganate used for oxidation. From this agreement it appears that the oxidation of sodium thiosulphate by permanganate, whether in an acid or in an alkaline solution, takes place according to fixed rules in the same manner, and that in this case it is suitable for finding a corresponding application for analytical purposes. If the quantities of oxygen required for the oxidation of a known weight of sodium thiosulphate are calculated, it is found that these quantities do not suffice to convert all the sulphur present into sulphuric acid. If, as experiment shows, the solution of permanganate effects a similar oxidation in the solutions of sodium thiosulphate, the quantity of the oxygen required for oxidation is smaller than that needed for converting all the sulphur into sulphuric acid, oxygen compounds of sulphur less rich in oxygen than sulphuric acid are formed at the same time. Sodium thiosulphate, both in acid and alkaline solutions, is therefore converted by permanganate into sodium sulphate and thiosulphate.

Quantitative Determination of Theobromine in Cacao Beans.—Dr. P. Jüss.—The "shaking-out" method is that which approximates most closely to the ideal determination of theobromine.

A Source of Error in the Determination of Phosphoric Acid with Magnesia-Mixture.—Dr. N. von Lorenz.—The error lies in the omission of citric acid when a little magnesia is simultaneously precipitated.

The Specific Weight of Aqueous Solutions.—G. Charpy.—(From the *Comptes Rendus*).

Relations between the Refraction of Gases and Vapours and their Chemical Composition.—J. W. Brühl.—Merely mentioned. (From the *Ber. Deut. Chem. Gesell.*).

Solubility of a Number of Salts in Acetone.—W. H. Krug and K. P. McElroy.—(From the *Four. Anal. Chem.*).

The Behaviour of Some Metals with Gases.—G. Neumann and F. Steintz (*Monatshefte für Chemie*).—This paper will be inserted in full.

Explanation of the Difficult Solubility of Chemically Pure Zinc in Acids.—Jul. Weeren (*Ber. Deutsch. Chem. Gesell.*).—Already inserted.

The most Suitable Form of the Gas-Volumeter.—G. Lunge (*Zeit. Angew. Chemie*).—For determinations of nitrous and nitric acid, the analysis of saltpetre, gun-cotton, nitroglycerin, and other esters and salts of nitric acid, the author uses a measuring-tube with a ball, the graduation of which begins at 100 c.c. and extends to 150 c.c. The tube is graduated into tenths of a c.c. All methods founded on the use of the appended flask, such as the analysis of chloride of lime, of manganese ore, permanganate, lead peroxide, the determination of nitrogen in ammonium salts, and in urea with sodium hypobromide, and of nitrogen in the diazo-compounds, can be effected with this apparatus. The determinations of carbonic acid in solids and liquids, with the aid of the author's generating-flask, the determination of carbon in iron and steel, and the standardising of acids for calcium carbonate, can also be effected with this apparatus. By appending Orsat's or Doyère Hempel's absorption-vessels the arrangement is made suitable for the analysis of smoke gases, in which two-thirds of the gas are left as a residue. For other gas analyses a tube holding 100 c.c. is recommended. In most cases the reduction-tube is to be arranged for moist gases by the introduction of a drop of water. For the analysis of nitrose, saltpetre, and dynamite, a dry reduction-tube is used. A measuring-tube holding 50 c.c. graduated from above downwards with a moist reduction-tube, and an especial shaking apparatus, suffices, in the author's opinion, for all the operations required in sulphuric acid works.

MISCELLANEOUS.

Bacteriology.—Mr. W. Heinemann has just issued a "Manual of Bacteriology" by Dr. A. B. Griffiths. It is a work for the laboratory, and contains an account of the latest researches on the subject. The subjects of nitrification, fermentation, ptomaines, germicides, &c., are fully described.

University College Chemical and Physical Society.—The Annual Public Meeting will be held at University College, on Friday, Feb. 24, 1893, when an address will be given by Prof. Watson-Smith, F.I.C., F.C.S., entitled "Diseases Incident to Work-People in Chemical and other Industries." The Chair will be taken at 8 o'clock by Prof. F. T. Roberts, M.D. There will be an exhibition of apparatus.

Recovery of Silver Residues.—R. Dietel (*Pharm. Zeitung*).—The residues are converted into silver chloride reduced with iron and dilute hydrochloric acid and washed until the chlorine reaction disappears. The silver, containing a little iron, is dissolved in pure nitric acid, the smaller portion is precipitated with boiling soda lye, and the precipitate is washed until a part of the filtrate leaves no residue. The larger portion is evaporated to dryness and then melted until the mass flows quietly. The melt is dissolved in water, filtered from the ferric oxide and slightly concentrated. Any nitrite formed is converted into nitrate by the addition of a small quantity of nitric acid. If the solution is coloured yellow in consequence of the presence of a small quantity of ferric nitrate, the silver oxide mixed with iron oxide, obtained by the treatment of the smaller part of the silver solution, is added, and the whole is boiled until both are transformed into silver nitrate and ferric oxide, *i.e.*, until a filtered and diluted portion gives with potassium ferrocyanide a pure white flocculent precipitate or turbidity. The whole is evaporated to dryness, taken up in water, and again evaporated to dryness.

MEETINGS FOR THE WEEK.

- MONDAY, 13th.—Medical, 8.30.
— Society of Arts, 8. "The Practical Measurement of Alternating Electrical Currents," by Prof. J. A. Fleming, F.R.S. (Cantor Lectures).
- TUESDAY, 14th.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8. (Anniversary).
- WEDNESDAY, 15th.—Society of Arts, 8. "The Detection and Estimation of Small Proportions of Inflammable Gas or Vapour in Air," by Prof. Frank Clowes.
— Meteorological, 7.
— Microscopical, 8.
- THURSDAY, 16th.—Royal, 4.30.
— Royal Institution, 3. "The Factors of Organic Evolution," by Prof. Patrick Geddes.
— Society of Arts, 3. "The Progress of India Under the Crown," by Sir William Wilson Hunter, K.C.S.I., C.I.E.
— Chemical Society, 8. Ballot for the Election of Fellows. "Platinous Chloride," by W. A. Shenstone. "Melting-points of Compounds of Similar Constitution," by Dr. Kipping. "Electrolysis of Iodic Ethylic Camphorall," by Dr. Walker. "New Base from *Corydalis cara*," by Dr. Dobbie and A. Lauder.
- FRIDAY, 17th.—Royal Institution, 9. "Turacin, a Remarkable Animal Pigment containing Copper," by Prof. A. H. Church, M.A., F.R.S.
— Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.
— Geological, 3. (Anniversary).
— Quekett Club, 8. (Anniversary).
- SATURDAY, 18th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1734.

BEHAVIOUR OF THE GADOLINITE EARTHS WITH POTASSIUM CHROMATE

By G. KRÜSS and A. LOOSE.

IN reference to the feebly basic properties as they occur, especially in scandium, ytterbium, thulium, erbium, holmium, and terbium, the attempt was made to separate this portion of the rare earths from the more strongly basic samaria, didymia, and lanthana under such experimental conditions that the decomposability of the salts of the feebler bases should be increased as far as possible. This is attained if such bases are combined with feeble acids or an opportunity is afforded them of transformation in that direction.

Experiments on the action of potassium nitrite or potassium arsenite proved fruitless. The behaviour of the rare earths with neutral potassium chromate was, however, so remarkable that we wish to describe it. By means of this salt we may, according to the conditions of the experiment, precipitate from a solution of mixed earthy salts either the stronger or especially the feebler bases, and have thus at disposal a peculiarly effective agent for fractionation.

As the following experiments were to explain simultaneously the behaviour of the feeble and the stronger bases with potassium monochromate, an accidental initial material cannot be employed, in which all the earths might, indeed, according to spectroscopic observation, possibly be found, but a part of them might, perhaps, be especially accumulated. A material of yttria earth of medium basicity containing the weaker basic and erbia earths and, on the other hand, the stronger didymia earths in approximately equal quantities, seemed requisite for these experiments.

Production of the Initial Material.

After a part of the didymium and the erbium had been removed from the crude earths derived from the gadolinites of Hitteröe and Ytterby by fractionated precipitation with ammonia, according to G. Krüss (*Liebig's Annalen*, 265, 12), the intermediate fractions were put in hand in a nitric solution. In order to obtain an experimental material of known composition suitable for the intended purpose, the nitrate solutions were next treated with potassium sulphate as follows:—The concentrated solution was mixed with a concentrated solution of potassium sulphate, with the addition of crystals of potassium sulphate, and allowed to stand for two days. After filtration the slight red precipitate was washed with a cold concentrated solution of potassium sulphate, and the earths contained in the precipitate were again converted into nitrates. The filtrate from this first precipitate with potassium sulphate was again submitted to the same treatment with potassium sulphate; this second precipitate yielded a nitrate solution which showed the absorption lines of didymium faintly, but the erbium lines very strongly.

The filtrate from the precipitates of potassium sulphate was resolved into fractions by partial decomposition of the nitrates on heating, the earths of which represented a

R*, in which the first fraction (containing the feeblest

bases) was 105.59, second fraction 104.48, third fraction 100.08, fourth fraction 99.36, fifth fraction 98.2, and sixth fraction (containing the strongest bases) 97.3.

These numbers,* as well as the spectroscopic examination of these fractions, showed that by separating the filtrate from the potassium sulphate precipitates besides some ytterbia and erbia, yttria was chiefly removed, and this earth more uniformly mixed with the stronger as well as with the feebler bases could be obtained from the precipitates with potassium sulphate. Hence the first precipitate with potassium sulphate was submitted to the decomposition of the nitrate by heat.

The first fraction containing the most feebly basic constituents yielded on determining its equivalent a $R = 112.96$ and showed the following absorption-spectrum:—

λ .	Strength of absorption.	Symbol.
728.3.. ..	Faint	Dia
654.7.. ..	Rather distinct	Era
640.4.. ..	Very faint	Xa
579.2.. ..	Very faint	Di γ
536.3.. ..	Very faint	X γ
523.1.. ..	Very strong	Er β
485.5.. ..	Distinct	X δ
452.6.. ..	Fading	X ζ

The symbols used here and in the following memoirs are the same as those employed for the lines of the rare earths, producing absorption proposed by G. Krüss and L. F. Nilson (*Ber. Deut. Chem. Gesell.*, xx., 2134).

The second precipitation gave a $R = 110.74$, and the spectrum:—

λ .	Strength of absorption.	Symbol.
728.3.. ..	Sharp	Dia
654.7.. ..	Distinct	Era
640.4.. ..	Distinct	Xa
579.2.. ..	Fading	Di γ
542.6.. ..	"	X β
536.3.. ..	"	X γ
523.1.. ..	Broad and strong	Er β
485.5.. ..	"	X δ
452.6.. ..	Very broad and very strong.	X ζ

3. Fraction $R = 107.4$	All show the same spectrum, only the line 579.2 Di γ gradually increased in strength.
4. " " = 105.6	
5. " " = 104.57	
6. " " = 104.26	

The residue contained an earth $R = 102$, and on spectroscopic examination contained:—

λ .	Strength of absorption.	Symbol.
728.3.. ..	Strong	Dia
679.4.. ..	Rather strong	Di β
654.7.. ..	Faint	Era
640.4.. ..	Faint	Xa
626.1.. ..	Very faint	Di
579.2.. ..	Very strong	Di γ

* For the sake of perspicuity, a table of the basicity of the earths is here appended as resulting from the statements of numerous investigators; it is the foundation of the decomposition of the nitrates. The elements are so arranged that the series begins with the strongest bases and concludes with the feeblest. The atomic weights are appended according to the best determinations:—

Element.	Atomic Weight.
Lanthanum	138.88 (Brauner, 1882); 138.01 (Cleve, 1883).
Didymium	146.58 (Brauner, 1882; also Nilson & Petterson).
Samarium	150.02 (Cleve); 150.7 (Brauner).
Yttrium	88.9 (Cleve); 188.2, 8.902; 187.4, 89.5.
Terbium	159.48 (Lecoq de Boisbaudran, 1890).
Holmium	160 (Cleve, 1879).
Erbium	166 (Cleve, 1880).
Thulium	170.7 (Cleve, 1880).
Ytterbium	173 (Nilson, 1880).
Scandium	43.98 (Nilson, 1885; and Robinson, 1884).
Cer. as CeO ₂	139.87 (Brauner, 1885; and Robinson, 1884).

λ .	Strength of absorption.	Symbol.
536'3.. ..	Very faint	X γ
523'1.. ..	Strong	Er β
512'2.. ..	Rather strong	Di ϵ
482	Distinct	Di ζ
477'7.. ..	Fading	Sm β
469	Distinct	Di η
463'2.. ..	Rather strong	Sm β
452'6.. ..	Very strong	X ζ
445'1.. ..	"	Di δ
428'5.. ..	Strong	X η
409	"	Sm β

* Subsequently occur together.

This last portion of the earths worked up after a considerable elimination of yttria, by separating the filtrate of the potassium sulphate precipitates and removal of an excess of erbium and samarium oxide by the first filtering off of the potassium sulphate precipitates still contained sufficient of the latter earths, as well as holmium and didymium earths in approximately equal quantities (judging by the spectrum). At the same time, these earths were still accompanied with considerable quantities of

earths of medium basicity of yttria ($Y = \text{about } 90$), as may be seen from $R = 102$.

Exactly the use of such a mixed material, the approximate composition of which is determined by preliminary experiments, will best show the *modus operandi* of the method employed. Hence, this last mentioned material

with a $R = 102$, and the spectrum given in the last table is used as material for the following researches.

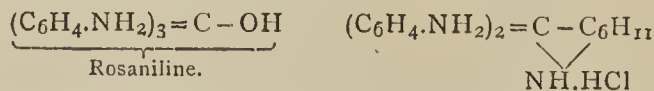
(To be continued).

RESEARCHES ON THE ACID SALTS, AND THE CONSTITUTION OF THE COLOURING MATTERS OF THE ROSALINE GROUP.

By M. A. ROSENSTIEHL.

1. If we are at present quite decided as to the constitution of the bases of the rosaniline group, it is not the same with the bodies which we consider as their salts, and which as colouring matters have acquired an importance of the first rank. I call to mind that according to the classic researches of A. W. Hofmann, rosaniline is the hydrate and magenta the hydrochlorate of a hypothetical triamine, $C_{19}H_{17}N_3$.

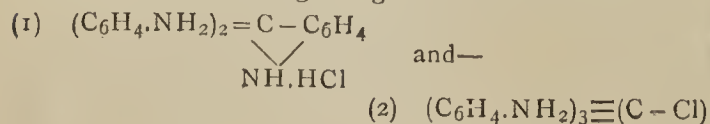
E. and O. Fischer, after having discovered the true constitution of rosaniline, and characterising it as triamido triphenylcarbinol, have thought it well to retain Hofmann's hypothesis for the constitution of magenta, and have established the following relation between these two bodies:—



That is to say, after having defined the part which belongs to oxygen in the mol. of rosaniline, they do not assign a corresponding function to the chlorine of magenta. According to them it is combined with Hofmann's hypothetical amine in the state of hydrochloric acid.

The object of this paper is not to discuss the reasons for the prevalence of an interpretation, which is neither logical nor simple, but to give the experimental proof that magenta and its congeners, in place of being salts of an amine, are ethers of aromatic amido-alcohols.

2. This manner of regarding the two formulæ—



we see that the former corresponds to a diamine which should be able to unite with 2 mols. of acid, whilst the second contains three times the group NH_2 , and corresponds to a body which ought to fix 3 mols. of acid.

We know that A. W. Hofmann has prepared and analysed an acid salt of rosaniline which he considers as a trihydrochlorate. This fact would seem to decide the question in favour of formula (1). But if we examine the original memoir (*Proc. Roy. Soc.*, vol. xii., p. 8) we find that Hofmann's affirmation rests upon an interpretation rather than upon precise facts. The analyses, moreover, have not been published. In the saturated salt of a triamine he could not at his epoch see anything but a triacid salt.

3. If we try to prepare the acid trihydrochlorate in a state of purity, according to Hofmann, we easily understand the nature of the difficulty. The hygrometric salt only abandons its water on losing acid. Nevertheless, analysis always shows more chlorine than is required for 3 atoms, but less than 1 mol. to 4 atoms of chlorine.

Only one of these salts, the hydrobromate of hexamethylated rosaniline violet, has been obtained pure by the evaporation of its aqueous solution on the water-bath. A substance of this nature, $C_{20}H_{15}(CH_3)_4N.4HBr_4$, was obtained in 1877 by Brauner and Brandenburg (*Berichte*, vol. x., p. 1845). For the others the moist way had to be abandoned. The colouring matters in the state of chlorides or bromides absorb dry gaseous HCl or HBr , with evolution of heat. Sometimes there occurs fusion,—an accident which must be prevented by mixing the hydracid gas with dry air.

The colouring matters increase in weight, and the quantity of acid absorbed is much greater than necessary to satisfy the chemical affinities. But we obtain compounds of a constant composition by placing the supersaturated matters in a vacuum in the cold over concentrated sulphuric acid. After two or three days the weight no longer varies. The same result is reached more rapidly on exposing the substance in a current of cold dry air.

4. The polyacid salts no longer possess the metallic lustre so characteristic of the colouring matters whence they are derived. Those of rosaniline are not stable; after a few days water no longer dissolves them without residue. The methylic derivatives appear most stable. The aqueous solution possesses the colour of the original colouring matters. But, if instead of dissolving them in water they are allowed to become moist in contact with air, and spread out in a slender layer upon a white saucer, the characteristic colouration of the acid salts appears. The salts of magenta and of malachite green are yellow.

6. The examination of the analytical results leaves no doubt as to the conclusions to be drawn. Triamidic triphenylcarbinol, whether methylated or not, produces acid salts containing 4 atoms of bromine or chlorine; the same tetramethylated diamide carbinol gives rise to salts containing 3 atoms of chlorine or bromine for 2 atoms of nitrogen.

With regard to acids rosaniline and its congeners present two distinct functions: an alcohol function and an amine function. Experiment shows that the alcoholic function predominates, though modified by the propinquity of the group NH_2 . The basic character is thus increased. The properties of the bases are comparable to those of the metallic protoxides.

The fact is that these amidic ethers undergo double decompositions with the same ease as the mineral salts. They are intermediate between the alkaline bases and the alcohols.

The amine function takes the second rank. We must insist upon this point, that the rosaline is not a triamine,—that function belongs to its ether. In consequence of the presence of the acid radicle in its molecule, the amine character is diminished, and we readily understand the relative instability of these salts.

In fine, if Hofmann has clearly seen the two series of compounds which the acids form with rosaniline, the extreme instability of the saturated salts on the one part and a preconceived idea on the other, did not permit him to recognise that polyhydrochlorate contains 4 atoms of chlorine. The establishment of the fact that 1 mol. containing 3 atoms of nitrogen may enter into reaction with 4 mols. of acid warrants us in concluding that we here encounter a novel function which we may characterise by saying that the colouring-matters of the rosaniline group are ethers of the amidic tertiary aromatic alcohols.—*Comptes Rendus*, vol. cxvi., p. 194.

ON THE GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 71).

II.—Action of Hydrogen on Hot Glass.

A CURRENT of hydrogen, purified by being passed through a red hot tube full of copper-wire gauze (*vide supra*) was passed through a U-tube containing vitrioled pumice, thence through a combustion tube 300 m.m. long and 15 m.m. wide inside, which was kept at a red heat by means of a combustion furnace, and, from this tube, into a graduated Pisani bottle; and this operation was continued until we felt sure from the volume of gas collected that the hydrogen, as it came out of the combustion tube, must be as free as at all possible, of both water and oxygen (its liability to be contaminated with sulphurous acid was not yet known to us at the time). We then attached to the outlet of the combustion tube two U-tubes charged with vitrioled pumice, of which the first was tared. From the second the gas passed into the Pisani bottle to be measured there. The experiment was continued until 12 litres of hydrogen had passed through the tared U-tube, which was then detached and weighed. In the first four experiments the combustion tube was empty; in the fifth it was filled with fragments of combustion tubing; in the sixth the combustion tube was in the condition in which it had been left by the preceding experiment.

The results were as follows:—

	Experiment—					
	I.	II.	III.	IV.	V.	VI.
Time allowed for the 12 litres passing through	2'5	1'5	3	3'25	3'50	3'5 hours.
M.grms. of water obtained..	0'4	3'0	0'9	5'0	10'3	5'3 "

Experiments I. and III., as we see, yielded practically no water (in No. III., indeed, the U-tube lost 0'9 m.grm.); the 3 m.grm. in Experiment II. may be accounted for by the gas having passed through very rapidly, but the 5 m.grm. produced in Experiment IV. cannot thus be explained away. Suspecting that the water produced in the copper gauze tube had not been completely retained by the U-tube provided for the purpose, we inserted a tared U-tube with vitrioled pumice after it, before proceeding to Experiments V. and VI.; but this additional tube gained only 0'9 m.grm. in V. and 0'8 in VI. The obvious irregularities in the results are probably owing to a small quantity of sulphurous acid produced in the U-tube following the copper gauze; but as this U-tube was only small, we have little doubt that the 10'3 m.grm. of water obtained in V. were at least partly produced by the action of the hydrogen on the hot glass. Admitting this, the fact that only 5'3 m.grm. were obtained in Experiment VI. is easily explained: the available stock of oxygen in the

skins of the fragments had been largely exhausted by Experiment V. We will resume these experiments with perfectly oxygen-free hydrogen, such as we subsequently learned to prepare, as soon as we can find the time, because it is important to know whether or not red hot glass is absolutely proof against hydrogen.

III.—Syntheses of Water effected with Small Weights of Oxide of Copper.

Referring to the section headed "Our First Series of Syntheses" (and to Fig. 3) for a description of our apparatus and exact mode of operating, we at once pass to a statement of our results. A glance at the table shows that Experiments I. and II. were absolute blanks, having been made with an empty reduction tube. Under "Oxygen used" we give the loss of weight suffered by the oxide of copper, uncorrected for the displaced air. From it the "water due" is calculated by multiplication with 1'12537 (see under "First Series of Syntheses"). "Surplus hydrogen" means the number of litres of hydrogen which were collected in the "Pisani" bottle while the gas streamed through the hot reduction tube, uncorrected. "Water obtained" means the total weight of water obtained, uncorrected for the displaced air.

	Experiment—				
	I.	II.	III.	IV.	V.
Oxygen used, m.grms.	0	0	291'95	324'52	415'8
Water due	0	0	328'6	365'2	467'93
Surplus hydrogen used, litres..	5	3	10	10	9'5
Water obtained, m.grms. ..	0'6	0'25	327'5	366'9	467'9
Surplus water ..	0'6	0'25	—1'1	1'7	—0'03

	Experiment—				
	VI.	VII.	VIII.	IX.	X.
Oxygen used ..	426'88	4230'25	2876'45	4805'25	621'2
Water due..	480'41	4760'6	3237'1	5407'6	699'08
Surplus hydrogen used ..	9'5(?)	3	3'5	3	5
Water obtained .	480'35	4761'1	3235'9	5406'6	700'3
Surplus water ..	—0'06	0'5	—1'2	—1'0	1'22

Supplementary Experiments.

XI. In this experiment the "Oxygen used" amounted to 411'9 m.grms., and the reduction was effected with the least sufficient volume of hydrogen. The water obtained weighed 463'6 m.grms.; that is to say, 0'06 more than $411'9 \times 1'12537$. After the apparatus had been weighed, the parts were again put together, the copper was heated in a litre of hydrogen to make sure of its freedom from oxygen of any kind; only then the water-absorption tubes were appended, and the experiment continued until 10 litres of hydrogen had gone over the heated metal. Of the two vitrioled pumice tubes which followed the reduction tube, the first lost 4'45, the second gained 5'05 m.grms., which anomaly we were not able to explain, and perhaps we had no right to look upon the net gain of 0'6 m.grm. as representing the adventitious water produced from these 10 litres of hydrogen.

XII. Essentially a repetition of No. 11, except that only 3 litres of hydrogen were used in the second stage. "Oxygen used" = 474'35 m.grms.; water due = 533'64; water got = 534'4; excess = 0'57 m.grm. In the second stage the anomaly noticed in No. XI. again presented itself; the first of the vitrioled U-tubes lost 2'6 m.grms., the second gained 3'3; net gain = 0'7 m.grm.

XIII. The copper resulting from XII. was left in the tube over night; it was then re-heated in 3 litres of hydrogen, the water absorption tubes attached, and the experiment continued until 11 litres of hydrogen had gone through the apparatus. The first U-tube lost 2'65 m.grms., the second gained 2'55; net loss = 0'1 m.grm.

XIV. Oxygen used = 609'55 m.grm., water due =

* *Proceedings of the Philosophical Society of Glasgow.*

685.97; water obtained = 686.30; excess = 0.33 m.grm. In the second stage 12 litres of hydrogen were used, the adventitious water amounted to $-1.55 + 2.8 = 1.25$ m.grm.

XV. and XVI. In these experiments the oxide of copper tube was omitted, and its place taken by a somewhat smaller tube drawn out at both ends, and charged with a scroll of platinum foil. The platinum was heated in the hydrogen for a whole hour before the U-tubes for the absorption of water were attached. The hydrogen from the copper gauze tube passed through two successive U-tubes charged with vitriol pumice, and the platinum tube was followed by two similar tared U-tubes (1 and 2), and these again by a protection tube to keep out the vapour of water from the Pisani bottle.

	Experiment—		
	XV.	XVI.	XVI.A.
Hydrogen used.. ..	10	11	12 litres.
Gain of U-tube 1 ..	1.5	1.0	1.7 m.grms.
Gain of U-tube 2 ..	0.2	-0.15	0.1 m.grm.
Total water produced	1.7	0.85	1.8 m.grms.

XVII. and XVIII. In these experiments an empty tube was substituted for the one containing the platinum foil; the procedure otherwise was the same as in the case of XV. and XVI.

	Exp. XVII.	Exp. XVIII.
Hydrogen used.. ..	10	10 litres.
Gain of U-tube 1 ..	1.1	1.3 m.grms.
Gain of U-tube 2 ..	-0.2	-0.5 m.grm.
Total adventitious water	0.9	0.8 m.grm.

At the time when these nineteen experiments were made, we were still in ignorance of the fact that even in the cold hydrogen acts perceptibly on oil of vitriol with formation of sulphurous acid. We were, therefore, quite at a loss to explain the anomaly which presented itself in some of them, that certain U-tubes, which ought to have remained constant or gained weight, lost weight. On the whole, however, we took them as proving that in a synthesis of water carried out with, say 8 grms. or more, of oxygen, the adventitious water produced in the reduction tube amounts to very little provided the hydrogen which enters the reduction tube is really free of oxygen; and ours, we thought, was, because we had passed the gas through a tube full of red hot copper gauze, followed by one or two U tubes charged with vitriol pumice.

(To be continued).

MAGNESIUM ZINC-EISEN.

By H. N. WARREN, Research Analyst.

THIS compound intended solely for pyrotechny is produced either by the electrolysis of magnesium sodium chloride in contact with zinc, or by the action of sodium metal upon that compound. As in the first instance, about ten or twelve pounds of zinc are introduced into a convenient size plumbago crucible, through the bottom of which is inserted a carbon rod; an excess of sodium magnesium chloride is next added, and a current of about 50 volts passed through the whole. The zinc speedily absorbs the magnesium thus set free, while chlorine escapes abundantly from the further electrode in contact with the magnesium chloride.

When an alloy containing about 70 per cent of magnesium has been obtained the current is broken, and a small quantity of ferrous chloride introduced; a further action is thus established, metallic iron being set free, which further alloys with both the zinc and magnesium to the extent of about 12 per cent. By this means a compound is obtained possessing so brittle a texture as to be readily reduced to the finest powder.

In the second instance, a saturated alloy of sodium and zinc is caused to act upon a mixture of magnesium sodium chloride; the sodium speedily changes place with the magnesium, forming the above mentioned alloy, to which an equivalent portion of iron is introduced by the action of ferrous chloride. These alloys are invaluable in photography, for flash-light, and in pyrotechny as signals, being equal to the pure magnesium as a light producing agent, at the same time being produced at a much lower cost.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

INDUSTRIAL APPLIANCES FOR ELECTROLYSIS OF METALLIC CHLORIDES AND THE OBTAINING OF CHLORINE AND PURE METAL IN A CONTINUOUS MANNER.*

As we know, chlorides can be decomposed by means of a pile current into chlorine and metal. Thus, Bunsen obtained magnesium, then with Mathiessen, barium, strontium, and calcium, by conveying a current of proper intensity into the melted chlorides. H. Ste.-Claire Deville also applied this method with great success to aluminium by treating double chloride of aluminium and sodium.

According to these principles the new apparatus is formed of—

1. A prismatic vat (the shape of which can be altered according to circumstances) of cement on an iron skeleton; the cement can be replaced by substances also refractory to acids.

2. A bell-shaped cap of cement resting on a channel, on the top part of the vat; it dips partially into the electrolyte, so as to assure a perfect hydraulic joining formed by the electrolyte itself.

3. This cap has a pipe for the evolution of chlorine. The electrolytic apparatus being formed by several vats, their evolution pipes all run to a chief conduit, which conveys the chlorine into the apparatus, where it is industrially treated.

Special appliances render a rapid dismantling possible. The cap is raised by means of a crane, and the lead pipe taken from the chief conduit by a movable nut of hardened lead fitted to a special cock.

4. Anodes of agglomerated graphite, artificially made if necessary, by putting cast iron in contact with coal. The current can be taken from the vat either outside or inside.

5. Cathodes formed of thin plates of lead in double sheets, laid crosswise on metallic sheets fixed permanently in the vat; the current is conveyed by these fixed plates.

6. Electrodes arranged at a certain distance from the bottom of the vat in order to avoid interior short circuits in the case where the conductive substances happened to fall to the bottom of the vat, thus re-uniting two neighbouring electrodes.

7. Lead pipes forming fixed cathodes arranged along a rectangular surface constituting a flat serpentine; they take in the vat the place of a certain number of cathodes; they are protected against the action of the chlorine dissolved in the electrolyte by the electrolytic current itself; for they constantly remain in communication with the negative pole.

8. Lead pipes arranged between the different vats uniting them in two's, so as to preserve the condensation degree of the liquid constant by a continuous circulation of the electrolytic solution of the metallic chloride.

9. Tubes on the inside of the receivers intended to expel

* Bulletin International de l'Electricité, Jan. 16, 1893.

the chlorine, by means of a current, as also the air, before the opening of the vat.

10. The parts susceptible of being attacked by chlorine are placed in the centre of the electrolytic bath and protected by the current of the negative pole.

11. A special cock of hardened lead, which enables the dismounting of the vats easily and without loss of chlorine.

12. Vats kept out of reach of the exterior air by wooden cases; the interval between the cases and vats is filled by some substance which is a bad conductor of heat, such as sawdust, wool, &c.

ANALYSIS OF GADOLINITE. (FROM LLANO COUNTY, TEXAS).

By L. G. EAKINS.*

SiO ₂	23.79
ThO ₂	0.58
Fe ₂ O ₃	0.96
Ce ₂ O ₃	2.62
(DiLa) ₂ O ₃	5.22
(YEr) ₂ O ₃	41.55
FeO	12.42
GlO	11.33
MnO	trace
CaO	0.74
MgO	trace
Alkalies..	trace
H ₂ O	1.03
P ₂ O ₅	0.05

100.29

In the rare earths from this mineral the absorption spectrum of didymium was strong, and that of erbium was weak. The molecular weight of the oxide (YEr)₂O₃ was 260.—*Bulletin of the United States Geological Survey*, No. 64.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 19th, 1893.

Prof. A. CRUM BROWN, President, in the Chair.

MESSRS. James W. Rodger and Morris W. Travers were formally admitted Fellows of the Society.

Ordinary certificates were read for the first time in favour of Messrs. William Thomas Boone, 6, Mount Pleasant Road, Tottenham; Frederick George Fuller, 19, Brunswick Square, W.C.; Arthur John Heath, 1, Grove Villas, Redland, Bristol; Wesley Lambert, 55, Plumstead Common Road, Plumstead; Herbert Bloome Mole, Hill-side, Shepton Mallet; Fred. Marsden, Bangor, North Wales; Charles Platt, Buffalo, N.Y., U.S.A.; Charles Henry Southwell, Boston; John Charles Umney, 50, Southwark Street, London; Herbert Wills, LL.D., Fern Bank, Halliwell, near Bolton.

Certificates of the following candidates, proposed by the Council under Bye-law I., para. 3, were also read:—Francis P. Dunnington, Charlottesville, Va., U.S.N.A.; Albin Haller, 14, Rue de Metz, à Nancy; William J. Martin, jun., M.D., Charlottesville, Va., U.S.N.A.; Charles E. Wait, Knoxville, Tenn., U.S.N.A.; Wilmoughby Walke, Fort Munroe, Va., U.S.N.A.; Henry C. White, Athens, Georgia, U.S.N.A.

* Compare Hidden and Mackintosh, *Ann. Journ. Sci.*, Dec., 1889.

Address to M. Pasteur.

On behalf of the Chemical Society of London, we, the President and Officers, beg to tender to you, Mons. Pasteur, our most hearty congratulations on the occasion of your 70th birthday, and to express the fervent hope that for many years to come you may continue to exert your beneficent influence over that department of scientific enquiry so peculiarly your own.

It is thirty years since you were elected a Foreign Member of our Society; and at that time your work as a pioneer was already completed. By your study of the tartaric acids and by the discovery of methods of resolving the optically inactive acid into its active components, you laid the foundation of the modern theories of geometrical isomerism which during recent years have served so largely to promote new and important experimental enquiries; and you placed weapons in the hands of chemists which have retained their usefulness up to the present day, and which over and over again have been wielded with marvellous effect.

Furthermore, your studies on fermentations—apart from their industrial importance, which is immense—have served to promote enquiries of the utmost value to mankind, and their influence must ever be felt.

Few men have been able to present to the world so imperishable a record of services rendered to humanity; and your name is one which must ever be enshrined in loving memory in the records of time.

We are, Sir, in deepest respect,
Your most faithful colleagues,

A. CRUM BROWN.

T. E. THORPE.

HENRY E. ARMSTRONG.

JOHN M. THOMSON.

R. MELDOLA.

(Presented December 27, 1892).

Of the following papers those marked * were read:—

*93. "*Glucinum. Part I. The Preparation of Glucina from Beryl.*" By JOHN GIBSON, Ph.D.

Of the many methods proposed for the preparation of glucina from beryl, only a few give satisfactory results, and none of them can be applied easily on a large scale. The percentage of glucinum in beryl is small, and it is therefore necessary to work up large quantities of this very hard mineral in order to obtain a stock of glucina sufficient for the purposes of investigation. Hitherto it has been found necessary to grind the mineral to a very fine powder as a preliminary to its complete decomposition by the usual agents employed in the case of refractory silicates.

The present communication gives an account of a method by which a kilogram or more of beryl may be worked up at a time in an easy manner, and without being ground to a fine powder, the whole of the glucina contained in the beryl being obtained very quickly in a nearly pure condition, and, in particular, nearly free from alumina and oxide of iron. The method is based on the different behaviour of the fluorides of aluminium, iron, and glucinum when heated together, it being found that if coarsely ground beryl be heated in an iron vessel with six parts of ammonium hydrogen fluoride, the mineral is completely decomposed at a temperature below a red heat, the soluble aluminium fluoride at first formed being rendered insoluble in water if the heating be sufficiently prolonged, while the bulk of the fluorides of iron are decomposed and converted into ferric oxide, the glucinum fluoride remaining soluble in water.

A new method for the perfect removal of the last traces of iron from the crude glucina is also described, based on the observation that in the presence in solution of a large excess of a lead or mercuric salt the precipitation of the lead or mercury as sulphide by ammonium sulphide effects by mass action the complete precipitation of the iron.

*94. "The Determination of the Thermal Expansion of Liquids." By T. E. THORPE, F.R.S.

The author describes improvements in the ordinary dilatometrical method of determining the thermal expansion of liquids. The main improvement consists in the adoption of the simple device now employed in the construction of standard mercurial thermometers, *i.e.*, in enlarging the bore of the tube at some point in the stem, thus forming a small bulb or cavity in order that the position of the 0° and 100° points may be determined on each instrument irrespectively of its range without unduly increasing the length of the stem or diminishing the width of the scale divisions. The length of the stem is thus considerably shortened, so that both it and the thermometer can be wholly immersed in a bath of moderate size; this makes it possible to take successive readings with much greater rapidity than formerly, and obviates the necessity of correcting for the emergent columns of the two instruments, thereby diminishing the time and labour required both in the actual observations and the subsequent reductions.

In the paper the mode of constructing and calibrating the dilatometers is fully described, also the mode of cleaning and filling them, the baths used in heating them, and the method of making the observations.

DISCUSSION.

Professor RAMSAY having advocated the method of heating by means of the vapours of liquids boiling under regulated pressures which had been largely used by Prof. Young and himself in place of baths of heated liquid, Professor THORPE pointed out that the time occupied and labour involved in making the observations was small in comparison with that involved in their reduction, and that, for the purposes of calculation, it was very convenient to take readings at definite intervals of temperature; this, he thought, could be more readily done by means of a liquid bath.

Professor RAMSAY said that it was equally easy to vary and adjust the temperature of vapour baths, but admitted that such were not well adapted for use at low temperatures.

*95. "The Determination of the Thermal Expansion and Specific Volumes of Certain Paraffins and Paraffin Derivatives." By T. E. THORPE, F.R.S., and LIONEL M. JONES, B.Sc.

The authors give the data relating to a number of substances, and discuss the results, particularly in relation to Lossen's deductions. Their results are summarised in the Table.

It will be seen that, with the exception of that for propionic anhydride, all the observed numbers differ considerably from those calculated by means of Kopp's

values. On the other hand, they show in the main a fairly satisfactory agreement with the values calculated by Lossen's formula. It is noteworthy that the observed value for acetic anhydride deduced from Kopp's experiments, *viz.*, 109.9, is also greatly in excess of the value calculated by Lossen's formula. If, however, Lossen's slightly higher value, *e.g.*, $\text{CO}_2\text{H} = 10.74$, as given for the oxalic ethers, be taken, values for these oxides are obtained which are in better agreement with the results of observation; thus—

	Observed.	Calculated.
Acetic anhydride	109.9	108.4
Propionic anhydride ..	154.2	154.4

*96. "The Hydrocarbons Derived from Dipentene Dihydrochloride." By WILLIAM A. TILDEN and SYDNEY WILLIAMSON.

The dihydrochloride $\text{C}_{10}\text{H}_{16}\text{Cl}_2$ (m. p. 50°), prepared by the interaction of moist hydrogen chloride and dextro- or levo-rotatory turpentine, is known to be identical with the dihydrochloride formed from dextro- or levo-rotatory citrene (limonene) or from inactive "dipentene." The hydrocarbon obtained by removing the elements of hydrogen chloride from this compound has been supposed to consist essentially of one compound, dipentene, but in view of results obtained in oxidising this substance (*Trans.*, liii., 880), a further examination of the product seemed desirable.

The authors find, by direct experiment, that, like dextrolimonene, when oxidised by nitric acid, levulimonene and pure dipentene afford neither toluic nor terephthalic acid. The product obtained by heating dipentene dihydrochloride with aniline, however, is a mixture of hydrocarbons, of which dipentene is perhaps the most abundant constituent, but is accompanied by large proportions of cymene, terpinene, terpinolene, and a small quantity (about 2.5 per cent) of a saturated paraffinoid hydrocarbon boiling at about 155°. The toluic acid obtained in the former experiments (*loc. cit.*), therefore, is not to be regarded as formed from dipentene, but from the cymene present, and to some extent from the terpinene, which, when oxidised by nitric acid, yields a smaller but appreciable amount of this acid.

The paper concludes with a short discussion of some theoretical points, having reference chiefly to the formulæ which have been ascribed to pinene and camphene.

*97. "Sulphonic Derivatives of Camphor." By F. STANLEY KIPPING, Ph.D., D.Sc., and W. J. POPE.

The study of these compounds has been entered upon in order, if possible, to throw light on the changes which attend the formation of acetylorthoxylene, &c., from camphor and sulphuric acid (*cf.* Armstrong and Kipping, *Trans.*, 1893, 75).

	B. p. ° C.	Density at 0°.	Density at b. p.	Specific volume.		
				Obs.	Kopp.	Lossen.
Pentane	36.3	0.64750	0.61200	117.6	121.0	117.2
Isopentane	30.4	0.63872	0.60857	118.3	121.0	117.2
Isohexane	62.0	0.67660	0.61744	139.3	143.0	139.8
Amylene	36.4	0.68499	0.64759	108.1	110.0	109.7
Isoprene	35.8	0.6912	0.6545	103.9	99.0	102.3
Trimethyl carbinol ..	82.2	0.80716	0.7194	102.8	106.8	102.0
Dimethyl ethyl carbinol ..	101.3	0.8269	0.7248	121.4	128.8	123.4
Inactive amyl alcohol ..	131.4	0.82536	0.71362	123.3	128.8	123.4
Active amyl alcohol ..	128.7	0.83302	0.72111	122.0	128.8	123.4
Methyl ethyl ketone ..	80.6	0.82961	0.74422	96.7	100.2	95.1
Methyl propyl ketone ..	101.7	0.82585	0.72568	118.5	122.2	117.2
Diethyl ketone	102.1	0.8335	0.7306	117.7	122.2	117.2
Propionic anhydride ..	168.6	1.0336	0.8431	154.2	53.2	150.3
Methyl sulphide	37.5	0.87022	0.82567	75.1	77.6	75.8
Isobutylene bromide ..	149.6	1.7675	1.5147	142.6	144.2	142.8

The preparation of camphorsulphonic acid has been attempted by several chemists, but up to the present with a uniform lack of success; the authors found, however, that it may be prepared by the interaction of anhydrosulphuric acid containing about 15 per cent of anhydride and dry powdered camphor: very vigorous action ensues on adding the acid, much heat being liberated, and sulphur dioxide is evolved; on pouring the acid liquid on to ice, very little camphor separates. To purify the product, the sodium salt prepared from the solution is submitted to the action of phosphorus pentachloride, and, by a somewhat tedious process, *camphorsulphonic chloride*, $C_{10}H_{15}O \cdot SO_2Cl$, is obtained in colourless crystals which are a mixture of optically different modifications very difficult to resolve. The isolation of a pure sulphonic derivative of camphor in the manner described is by no means easy, several other products being simultaneously formed in large quantities.

According to Marsh and Cousins (*Trans.*, 1891, 967) camphorsulphonic acid is not formed by the interaction of chlorosulphonic acid and camphor dissolved in chloroform. The authors find, however, that camphor is readily sulphonated by chlorosulphonic acid in absence of a solvent; the action proceeds without any noticeable carbonisation or evolution of sulphur dioxide. The sulphonic chloride prepared from this product, like that already referred to, is a mixture of optically different isomerides.

What appears to be the pure dextrorotatory form of the sulphochloride crystallises in tetrahedra melting at $136-137^\circ$.

Prior to the isolation of the active chloride, the following derivatives were prepared from a nearly pure inactive product:—

Camphorsulphonamide, $C_{10}H_{15}O \cdot SO_2NH_2$, obtained by the action of aqueous or alcoholic ammonia on the sulphonic chloride; six-sided, transparent, colourless, monosymmetric plates ($a:b:c = 0.821:1:1.047$; $\beta = 81^\circ 4'$), melting at $134-135^\circ$.

Camphorsulphonic acid, $C_{10}H_{15}O \cdot SO_3H$. The sulphonic chloride is slowly hydrolysed by boiling water; the acid crystallises in arborescent forms, and is very deliquescent; it melts at $58-60^\circ$. Its aqueous solution dissolves zinc or magnesium with evolution of hydrogen; a series of well-defined salts has been obtained.

The action of anhydrosulphuric acid on the haloid derivatives of camphor is much less violent than when camphor itself is employed. Anhydrosulphuric acid dissolves bromocamphor with slight rise of temperature, giving an amber-coloured solution of sulphonic acid completely soluble in water. The sodium salt, prepared in the usual way, gives on treatment with phosphorus pentachloride a *bromocamphorsulphonic chloride*,—



which can be separated from a quantity of dark oil accompanying it by suitable methods. The purified substance crystallises from chloroform in magnificent octahedra, melting at $136-137^\circ$. The crystals are colourless and transparent, and may be readily obtained several centimetres in diameter.

Marsh and Cousins (*Trans.*, 1891, 974) have prepared a sulphonic chloride of similar composition by the action of chlorosulphonic acid on bromocamphor. They describe the substance as "a black semi-crystalline solid." A repetition of their work showed this substance to be merely an impure form of the one now described; the identity of the chlorides from the two sources having been established by the ordinary means and by crystallographic measurements. The chloride has a high rotatory power— $[\alpha]_D = \text{about } +128^\circ$ in chloroform solution.

Bromocamphorsulphonic acid, $C_{10}H_{14}BrO \cdot SO_3H$, is readily obtained by boiling the chloride with water. It forms large pyramidal shaped crystals, which are somewhat hygroscopic and very soluble in water. The anhydrous acid melts at $195-196^\circ$; the aqueous solution dis-

solves zinc and magnesium. The acid is described by Marsh and Cousins as a "black tarry mass." The salts generally crystallise well, and have been examined crystallographically. The *sulphonamide* crystallises in long silky needles, and melts at $144-145^\circ$.

Chlorocamphorsulphonic chloride, $C_{10}H_{14}ClO \cdot SO_2Cl$, obtained in an analogous manner, crystallises in massive colourless octahedra, indistinguishable in appearance from the bromo-derivative. It melts at $123-124^\circ$. $[\alpha]_D = \text{about } +110^\circ$ in chloroform solution. This substance was described by Marsh and Cousins (*loc. cit.*) as a "micro-crystalline black solid."

On boiling with water the chloride yields *chlorocamphorsulphonic acid*, $C_{10}H_{14}ClO \cdot SO_3H$, which crystallises in hygroscopic rectangular plates; it affords a series of well-defined salts.

The *ammonium* salts of bromo- and chloro-camphorsulphonic acids are especially interesting from a crystallographic point of view. Possessed of optical activity when in solution, they crystallise in monosymmetric prisms exhibiting hemimorphism and showing strongly marked pyroelectric properties.

The further investigation of these sulphonic derivatives, and of the by-products which are formed in their preparation, is in progress.

98. "The Preparation of Dinitro- α -naphthylamine [$NH_2:NO_2:NO_2 = 1:2:4$], from its Acetyl and Valeryl Derivatives." By R. MELDOLA, F.R.S., and M. O. FORSTER, Ph.D.

A simple method of preparing this compound was described by one of the authors in a note published in 1886 (*Ber.*, xix., 2683); other investigators having experienced difficulties, or having altogether failed, in obtaining it by this method, we have been led to reinvestigate the subject, and can confirm the practicability of the process formerly described. The difficulty experienced by other workers has, no doubt, arisen from using the hydrolysing agent (sulphuric acid) either too strong or too weak. The following details may, therefore, be found useful:—

The α -acetnaphthalide is nitrated in glacial acetic acid in the usual way, using a little more than the theoretical quantity of fuming nitric acid. It will be found advantageous to divide the operation into two stages, adding one-half of the nitric acid to the well-cooled solution in the first place, and then allowing to stand over night, so that the mixed mononitro- α -acetnaphthalides are formed at a low temperature. The solution is warmed the following day in a water-bath till the crystalline mononitro-derivatives have dissolved up, when the other half of the nitric acid is added. The dinitro-derivative soon forms, and the solution begins to solidify while still hot. The whole mass forms a pulp of crystals when cold. The mother-liquor being squeezed out, the crystals are washed with water, drained, and purified by being boiled up with alcohol and allowed to cool. Very little of the dinitro- α -acetnaphthalide is lost by this treatment, as the compound is but slightly soluble in cold alcohol. Resinous impurities, which interfere with the purity of the subsequent product, are removed by the alcohol. The alcoholic extraction may be repeated if necessary. The purified dinitro-derivative, when dry, is easily hydrolysed by heating to the temperature of boiling water for about an hour with a mixture of equal volumes of strong sulphuric acid and water (50 grms. dinitro-compound, 150 c.c. strong sulphuric acid, and 150 c.c. of water). The product is poured into cold water, collected, washed, and crystallised from somewhat dilute alcohol with the addition of animal charcoal till it has the correct melting-point (237° from alcohol).

While engaged in these experiments, it appeared to be of interest to ascertain the effect of lighter and heavier acid radicles in facilitating or retarding hydrolysis by sulphuric acid. It was found that *formonaphthalide* could not be converted into a dinitro-derivative in glacial acetic

acid. Even when a large excess of nitric acid is used, the product is mononitroformonaphthalide. Nitrogen found: (I.) 13.08, (II.) 12.99 per cent; calculated for mononitro-derivative, 12.96 per cent; calculated for dinitro-derivative, 16.09 per cent.

It evidently consists of a mixture of isomerides, as no compound of a definite melting-point was isolated; much resin is also formed during the nitration.

Valeronaphthalide was prepared by boiling α -naphthylamine with excess of "anhydrous valerianic acid" (Hopkin and Williams) for at least thirty-six hours. The product fuses to an oil under hot water, and is purified by successive agitation with hot water, dilute ammonia, dilute chlorhydric acid (to remove unaltered naphthylamine), and finally with water. The resinous cake thus obtained gradually becomes a crystalline mass on standing in the cold. One or two crystallisations from dilute alcohol render the compound sufficiently pure for nitration. A specimen was purified for analysis by repeated alternate crystallisations from alcohol and benzene. The pure compound forms white silky needles melting at 125 to 126°, and gradually becoming violet on exposure to air and light: on analysis, it was found to contain 78.95 carbon, 7.72 hydrogen, and 6.25 nitrogen, the values calculated for $C_{10}H_7NH \cdot C_5H_9O$ being 79.29 carbon, 7.48 hydrogen, 6.17 nitrogen.

The nitration is easily effected by dissolving the substance in glacial acetic acid and at once adding to the cold solution a little more than the theoretical quantity of fuming nitric acid diluted with an equal volume of glacial acetic acid. It is best to start with a cold saturated solution of the valeronaphthalide in glacial acid. After adding the nitric acid, the solution may be allowed to stand for some hours in the cold and then warmed to 70–80° for about fifteen minutes. The nitration is complete by that time, the dinitro-derivative slowly separating out on cooling. The crystalline cake thus obtained is first washed with water and then purified by crystallisation from alcohol, in which the dinitro-derivative is much more soluble than the corresponding dinitro-acetnaphthalide. If, during nitration, decomposition sets in with effervescence, the contents of the vessel must be at once cooled, or the product will be found to be much contaminated with resinous matter, and the yield will be considerably diminished. Two experimental batches were lost by neglecting this precaution.

Dinitrovaleronaphthalide, when purified by crystallisation from alcohol and glacial acetic acid successively, forms pale straw coloured silky needles, having a melting point of 218°. It is rapidly converted into dinitro- α -naphthol by boiling with dilute alkali. A purified specimen was analysed with the following results:—Carbon 57.03, hydrogen 4.96, nitrogen 13.11. The values calculated for $C_{10}H_5(NO_2)_2 \cdot NH \cdot C_5H_9O$ being:—Carbon 56.78, hydrogen 4.73, nitrogen 13.24.

This compound appears to be more readily hydrolysed than the acetyl derivative. The proportions of acid, water, and substance found effective were:—30 grms. dinitro compound, 600 grms. strong sulphuric acid, 60 grms. water; after heating from 10–15 minutes in a water-bath, the product is precipitated by pouring the mixture into cold water and treating as in the case of the acetyl derivative. We have not made a series of exact comparisons between the acetyl and valeryl derivatives with the object of measuring the relative rates of hydrolysis. It appears, however, from our experiments, that valeryl is more easily removed than acetyl without deeper decomposition of the dinitro-derivative into resinous products, and this seems to point to the conclusion that there is an advantage in starting with a naphthalide containing a radicle heavier than acetyl. On the other hand, glacial acetic acid is so much cheaper than its higher homologues, that from an economical point of view the dinitro- α -acetnaphthalide will be found the most advantageous compound to employ for the preparation of dinitro- α -naphthylamine. It is proposed to prepare a

large quantity of the latter by the method described, with the object of extending our knowledge of the meta-derivatives of naphthalene, for the preparation of which the metadinitronaphthalene, obtained by the diazo-method, will, it is hoped, furnish a convenient source. We have received valuable assistance in conducting these experiments from Messrs. E. M. Hawkins and F. B. Burls, two of the third year students of the Finsbury Technical College, to whom we wish to express our thanks.

99. "Thionyl Bromide." By P. J. HARTOG and W. E. SIMS.

The authors have prepared thionyl bromide by the interaction of sodium bromide and thionyl chloride, obtaining it in the form of a deep crimson liquid of the relative density 2.68 at 18° C.; the colour is, however, possibly due to the presence of a small quantity of certain sulphur bromides: though their amount is small, hitherto it has not been found possible to deprive thionyl bromide of these impurities. At 150° thionyl bromide undergoes a complex decomposition, yielding bromine and sulphur bromides. It is extremely hygroscopic and must be preserved in sealed tubes.

100. "Desulphurisation of the Substituted Thioureas." By AUGUSTUS E. DIXON, M.D.

Some years ago (*C. S. Trans.*, 1889, 618) the author pointed out that certain disubstituted paraffinoid thioureas are not desulphurised when boiled with an alkaline solution of a lead salt: having since obtained data concerning a considerable number of thioureas, the following conclusions are drawn as to their behaviour with the agent in question:—

1. The monosubstituted thioureas are all desulphurised.
2. The tri- (and probably also the tetra-) substituted thioureas are not.
3. Disubstituted thioureas containing one or more benzenoid groups are desulphurised, but not if such groups be absent.

In the case of thioureas containing the allyl group, the results are less sharp than where alkyl residues are concerned; in the case of the former a trifling separation of lead sulphide is occasionally observed, but the amount produced varies from *nil* to enough to slightly darken the mixture; the effect in these cases is attributed to the difficulty encountered in obtaining the allyl derivatives in a pure condition.

The following compounds are described:—

sym.-*Diisobutylthiourea*, $CSN_2H_2(C_4H_9)_2$.—Colourless rhombic plates, melting at 87–88°.

Di-(sec.)-butylthiourea, $CSN_2H_2(C_4H_9)_2$.—Small colourless prisms, melting at 100–101° (uncorr.).

Methyl-(sec.)-butylthiourea, $CSN_2H_2(CH_3)(C_4H_9)$.—Flattened rhombic crystals, melting at 79–80°.

Ethyl-(sec.)-butylthiourea, $CSN_2H_2(C_2H_5)(C_4H_9)$.—Brilliant flattened crystals, melting at 57–58°.

Phenyl-(sec.)-butylthiourea, $CSN_2H_2(C_6H_5)(C_4H_9)$.—Long colourless needles; m. p. 100–101° (uncorr.).

Diisoamylthiourea, $CSN_2H_2(C_5H_{11})_2$.—Brilliant small white prisms; m. p. 72–73°.

Methylisoamylthiourea, $CSN_2H_2(CH_3)(C_5H_{11})$.—Beautiful vitreous rhombs; m. p. 75–76°.

Ethylisoamylthiourea, $CSN_2H_2(C_2H_5)(C_5H_{11})$.—White crystalline mass, melting at 45–46°.

Phenylisoamylthiourea, $CSN_2H_2(C_6H_5)(C_5H_{11})$.—Vitreous rhombic plates, melting at 101–102° (uncorr.).

(To be continued).

Kopp Memorial Lecture.—An Extra Meeting of the Chemical Society will be held on Monday, Feb. 20, at 8 p.m., the Anniversary of the death of Hermann Kopp, when a lecture will be delivered by Prof. Thorpe, F.R.S. The chair will be taken by Lord Playfair.

NOTICES OF BOOKS.

A Manual of Bacteriology. By A. B. GRIFFITHS, Ph.D., F.R.S., F.C.S. London: Heinemann, 1893.

THIS volume forms one of a series entitled "Heinemann's Scientific Handbooks," of which five volumes have already appeared. The author, Dr. Griffiths, is favourably known to the majority of our readers from the chemical and chemico-physiological papers which have appeared in the CHEMICAL NEWS, the *Comptes Rendus*, and elsewhere, as well as from his independent works.

By a remarkable and not altogether fortunate coincidence this volume has appeared almost simultaneously with Dr. P. F. Frankland's treatise, covering substantially similar ground and enforcing the same views.

In his opening chapter, the author gives Koch's four canons for deciding whether a micro-organism is the cause of any given disease. He then goes on to a survey of physiological experimentation, or as it is vulgarly called, vivisection, in which he concedes rather too much to that class of people whom the late Professor Sir Richard Owen aptly termed "bestiarious."

With the author's general nomenclature we find ourselves unable to agree. He restricts the name microbes to minute vegetable organisms, and even takes it as a synonym for bacteria. Now, if we look at the etymology we shall see that microbes or microbia are micro-organisms either of animal or vegetable character. He thinks that it must be to some extent consolatory to know that the disease germs which invade our bodies are not animals. We should find in this fact very little comfort. The only satisfactory circumstance is that plants have not yet been invested by our hysterical agitators with "equal rights." Were the germ of tetanus, *e.g.*, an animal, to destroy it with disinfectants would, perhaps, be denounced as an outrage. Their wonderful potentialities are explained in a very interesting manner.

In the second chapter, we have an account of the Edinburgh Bacteriological Laboratory and its fittings. This establishment works well considering its unfavourable environment. More fortunate is the Pasteur Institute in Paris, founded and endowed at the cost of £100,000.

In treating of the microscope, Dr. Griffiths recommends the monocular instrument. He suggests that a sheet of black paper should be placed near the eye not in use. We have found it very convenient to take a large old-fashioned spectacle frame, cover one of the glasses, for the eye which is not to be used, with a piece of black paper, and remove the other glass altogether.

Next we find the methods of cultivating microbia, the processes for staining, methods of mounting specimens, and the origin, classification, and identification of species.

Of course, on the origin of microbia little can be said. We have heard it surmised that they may have been conveyed from other worlds through the depths of space. This theory has the advantage that it cannot easily be either proved or disproved. It is, however, possible that if bacteria once landed on this terrestrial ball they may have repeated the invasion. We suggest this notion to epidemiologists as a hypothesis to account for new and mysterious diseases.

This work will be a valuable addition to the library of the hygienist.

Electrical Experiments. A Manual of Instructive Amusement. By G. E. BONNEY, author of "The Electro-Plater's Handbook," "Induction Coils," &c. With 144 Illustrations. London and New York: Whittaker and Co.

THIS work, dealing in a clear practical and, though popular, thoroughly sound manner with magnetism and

electricity, will doubtless meet with numerous and attentive readers.

The author teaches by the experimental method. He does not invite students to seek for definitions of magnetism and electricity, but lets them ascertain what these agencies can do and what they cannot do, and in this manner guides them to find out their nature better than by a "game at definitions."

The Principles of Theoretical Chemistry: with Special Reference to the Constitution of Chemical Compounds. By IRA REMSEN, Professor of Chemistry in the Johns Hopkins University. Fourth Edition, thoroughly Revised. London: Baillière, Tindall, and Cox. Philadelphia: Lea Bros. and Co., 1893.

THIS excellent and well-known treatise gives room for very little comment. It has been fully brought up to the present level of the science, and is enriched with an additional chapter on solution. Perhaps the only exception which may be legitimately taken to the work is that in expounding the periodic law the merit of Newlands is underrated, and that of Mendeleeff, and still more that of Lothar Meyer, exaggerated.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—The letter which has been addressed to me by Professor Thorpe, and which was sent by him for publication in your columns last week, has of necessity not yet come before a meeting of the Council of the Institute; but as the statement of his views has been given to the chemical world, I am compelled to request that, without delay, you will suffer me to correct what I consider to be an inaccurate rendering of what actually occurred at the last Council Meeting of the Institute, and of the inferences to be deduced therefrom.

The resolution, of which notice had been given, was moved by Dr. Teed as follows:—

"That in future the letters F.C.S. be omitted in the Register from all names of members of the Institute."

It was moved as an amendment by Mr. M. Carteighe, seconded by Mr. F. J. M. Page, and carried—

"That in future all letters indicating membership of any society except the Royal Society (London) be omitted in the Register from all names of Members of the Institute."

It was moved as an amendment by Professor T. E. Thorpe, seconded by Mr. R. J. Friswell, and lost—

"That all letters denoting membership of societies and degrees be deleted from the list of Members of the Institute."

It was moved as an amendment by Mr. A. H. Allen, seconded by Prof. T. E. Thorpe, and lost—

"That the words 'except the Royal Society (London)' be omitted."

The original amendment was then put as a substantive motion and carried.

From this it will be seen that the amendment which was carried finally as a substantive motion was brought forward by two gentlemen whom I am certain Professor Thorpe would be willing to recognise among those who have shown themselves zealous supporters of the present mode of election into the Chemical Society, and zealous friends of the Chemical Society. I will go further and say for myself that while in the Chair I have never exercised my right to vote except on the rare occasions when a casting vote has been required, but had I been on the

other side of the table on the occasion referred to, I should have voted for this amendment which covers the original motion. I state these facts in order to show that at least some of those whom he will, I trust, continue to recognise as his friends do not share his opinion in this matter, and that the action taken by the Council of the Institute is not the action of any section of its members.

The Council of the Institute *does* "know that it has no power to compel any of the Members of the Chemical Society to omit the letters F.C.S. after their names," but it has power over its register, and can regulate at will how many or how few letters it will admit there, and Professor Thorpe is on this point wrongly informed.

Professor Thorpe asserts that the Council of the Institute has put itself in an attitude of antagonism to the Chemical Society. This I emphatically deny. By thus calling public attention to the fact that he has decided to retire from the Institute, and in stating his reasons for retirement, Professor Thorpe forgets some important points in its history. At the Inaugural Meeting of the Chemical Society held in 1841, the objects of the Society were defined to be:—"The promotion of Chemistry and of those branches of Science immediately connected with it, by the reading, discussion, and subsequent publication of original communications, also the formation of a Chemical Library and Museum," and in the Charter the Chemical Society was declared to have been established "for the general advancement of Chemical Science."

Throughout the Charter and the bye-laws there is not one word relating to the election of Fellows which shows that any standard has at any time been set up by the Society by which the professional attainments of candidates for election could be estimated, and it is a matter of common knowledge that candidates of the most various qualifications are and have always been admitted into the Society. This being the case, a public meeting was held in 1876 at Burlington House, at which a committee was appointed to confer with the Council of the Society upon the question of establishing an organisation among chemists, which should stand toward the profession of chemistry in the same relation as that occupied by the Colleges of Surgeons and Physicians toward medicine. The result of the Conferences with the Council of the Chemical Society was that it was found impracticable for various reasons to establish a section of the Society for the purposes contemplated. Hence it became necessary to establish an independent association in the foundation of which some of the most distinguished Fellows of the Chemical Society were closely concerned.

The Association existed for some years under the Company's Acts and in 1885 received the Royal Charter. In the Charter of the Institute its object is defined to be not "the advancement of Chemical Science" by any direct operation, but in view of the importance of forming a body of "persons properly trained, and that their qualifications should be attested by certificates of competency," and seeing that "at present there is no institution or corporate body which has power to issue such certificates," the Institute was established.

As everybody knows, the persons who now constitute the Institute of Chemistry are on the one hand those who were originally incorporated as having rights to recognition, and on the other hand, younger men who are required to pass through a course of study extending over not less than three years and to pass certain examinations. The business of the Chemical Society, then, is to promote the study of chemical science; the function of the Institute is to carry out that which the Chemical Society could not do, namely, to register persons possessing certain well defined qualifications. When, therefore, Professor Thorpe states that "there is no greater inherent value or property in the letters F.I.C. than in those F.C.S." he is talking nonsense.

I am ready still to maintain, as I have done publicly, that the doors of the Chemical Society should remain open to the amateur, whoever he may be, who will engage

to subscribe faithfully to the declaration which every Fellow signs upon the occasion of his admission. But I think it may be questioned whether the use of the letters F.C.S. upon professional cards and in advertisements by *soi disant* analytical chemists is not a breach of their obligation. And when these letters come to be put forward by applicants for public appointments as evidence of professional qualification, it is time that the Council of the Chemical Society, to say nothing of the Institute, should take steps to prevent an imposition upon the public ignorance.

Can it be maintained that the use of letters under the present conditions of admission into the Chemical Society is necessary for the welfare of the Society, and the advancement of the high purposes it has in view? I think not. Else how is it that the other chemical societies of the world get on very well without them and the Physical Society of London, which is properly the sister society, prospers without any such addition?

It is a serious blow to the Institute that a man in the high position of Professor Thorpe should withdraw from its ranks, but his ardour in the cause of the great Society in which he holds the honourable office of treasurer has, I venture to think, led him to extend something less than justice to the efforts which are being made towards the satisfactory organisation of the profession. The influence which the leading scientific chemists might fairly be expected to exercise upon the proceedings of the Institute can only be exercised effectively while they remain members of that body. To withdraw is merely to leave the field to the enemy.

I must not conclude without explaining that this letter is addressed to you in my private capacity. Living, as I do, at a distance from London, I am placed at the disadvantage of being unable to confer, as I should have wished to do on such an occasion, with my colleagues, and I am desirous, therefore, of stating to them and to you that I do not profess now to be acting as the mouth-piece of the body of which I am temporarily President.—I am, &c.,

WILLIAM A. TILDEN.

Birmingham, Feb. 14, 1893.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—With reference to the letter of Professor Thorpe published in the *CHEMICAL NEWS*, vol. lxvii., p. 71, will you allow us, as the mover and seconder of the amended resolution referred to in that letter, to deny absolutely that it "is practically directed against the Fellows of the Chemical Society," as stated by Professor Thorpe.

No such feeling of disloyalty to the Chemical Society existed or exists in our minds, and it was because the majority of the Council held the same view that our *amended* resolution was passed instead of the original resolution.—We are, &c.,

M. CARTEIGHE.

FREDERICK JAS. M. PAGE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 5, January 30, 1893.

On Certain Articles of Copper of very Ancient Date derived from the Explorations of M. de Sarzec in Chaldea.—M. Berthelot.—Some of the articles found throw further light on the existence of a "copper age,"

prior to the bronze age. M. Berthelot has examined in particular a votive figure supposed belonging to an epoch prior to the Fortieth Century, B.C. The metal contained neither silver, bismuth, antimony, zinc, nor magnesium, but merely traces of lead, arsenic, and sulphur, along with a little lime and carbonates. It may be considered as copper, industrially pure. At its epoch bronze and tin were not yet worked either in Chaldea or Egypt.

The Pathogenic Properties of Soluble Substances Elaborated by the Microbe of the Contagious Peripneumonia of the Bovidae, and on their Value in the Diagnosis of the Chronic Forms of this Malady.—S. Arloing.—Cultures of the microbe from injection proved fatal to oxen within five to six hours, in the proportion of 0.064 grm. per kilo. of the living weight.

The H and K Rays in the Spectrum of the Solar Faculae.—G. E. Hale.—This paper will be inserted in full.

Decomposition of the Alkaline Aluminates in Presence of Alumina.—A. Ditte.—On contact with crystals of hydrated alumina, potassium aluminate is gradually decomposed and its alumina is separated as $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Gibbsite). The same phenomenon occurs with sodium aluminate. This explains the industrial process for preparing alumina from sodium aluminate by agitating a solution of this compound with the crystallised aluminium hydrate.

Electrometric Study of Acid Potassium Triplato-hexanitrite.—M. Vèzes.—This paper requires the insertion of the two accompanying graphic representations.

Action of Watery Vapour upon Ferric Chloride.—G. Rousseau.—There is a complete analogy between the decomposition of ferric chloride in vapour by gaseous water and that of its concentrated solutions. The products obtained in both cases at corresponding temperatures have the same compositions, have the same optical characters, and are similarly destroyed by the prolonged action of boiling water.

Two Combinations of Cuprous Cyanide with Alkaline Cyanides.—E. Fleurent.—The author obtains a blue compound, dicuprous-diammonium ammonium cyanide, $2\text{Cu}_2\text{Cy}_2 \cdot \text{CyNH}_4 \cdot 2\text{NH}_3 \cdot 3\text{H}_2\text{O}$, and a green compound, cupro-dicupric diammonium cyanide— $2\text{CuCy}_2 \cdot \text{Cu}_2\text{Cy}_2 \cdot 2\text{NH}_3 \cdot 3\text{H}_2\text{O}$.

The Composition of Some Hydrated Alkaline Phenates.—M. de Forcrand.—The author's results differ from those of Roméi.

Researches on the Acid Salts, and on the Constitution of the Colouring-Matters of the Rosaniline Group.—A. Rosenstiehl.—(See p. 76).

Analysis of Official Creosotes, Gayacol.—A. Béhal and E. Choay.—One of the two products in question, the creosote of wood-tar, is a complex mixture of phenols and phenolic ethers. The other, gayacol, is a definite chemical compound. The indications given for the analysis of the former kind are merely physical and colour reactions. The authors base their procedure on the following principles:—1. Hydrobromic acid completely demethylates at ordinary pressures the methylic ethers of the phenols. 2. The monophenols are easily carried away by a current of steam. 3. A current of steam does not appreciably remove the polyphenols. 4. Ether entirely removes pyrocatechine and homopyrocatechine from an aqueous solution, and also removes the monophenols. 5. Benzene separates almost quantitatively pyrocatechine from homopyrocatechine. Pure gayacol is a white crystalline solid, melting at 28.5° and boiling at 205.1° .

Apparatus for Estimating Precipitates by an Optical Method.—E. Aglot.—This paper will be inserted in full.

The Pre-Existence of Gluten in Wheat.—M. Balland.—The author refutes the hypothesis of Weyl and Bischoff that gluten is formed by the simultaneous action of water and ferments.

Zeitschrift für Analytische Chemie.

Vol. xxxii., Part I.

Modified Forms of Berthelot's Calorimetric Bomb.—Scheurer-Kestner, Meunier-Dollfus, and Pierre-Mahler (*Bull. de Mulhouse and Comptes Rendus*).—This paper requires the five accompanying figures.

A Refractometer.—E. H. Amagat and F. Jean (*Beiblätter zu den Annalen der Physik und Chemie*).—The apparatus depends on the same principle as the liquoscope of Soudén, i.e., the deviation of a mark observed through a prism filled with the liquid in question.

An Improved Thermo-Column.—M. Gülcher (*Berg. und Hutten Zeit.*).—The instrument is durable, cheap, and not exposed to injury from a sudden increase of gaseous pressure.

Working with the Filter-Press.—H. Wilde (*Chem. Zeit.*).—The author combines with the filter-press a cylindrical pressure vessel which can bear a pressure of several atmospheres.

A Shaking-Machine.—W. R. Dunstan and T. S. Dymond.—(From the *CHEMICAL NEWS*).

A New Air Bath.—Maunsel White and F. R. Bennet.—(From the *Four. Anal. Chem.*).

Fusion Cones.—Cramer (*Thon-Industrie*).—These cones are devised to indicate the temperatures reached in brick burning.

The Presence of Hypochlorous Acid in Chlorine Water obtained from Chloride of Lime and Hypochlorous Acid.—K. Kock.—Hypochlorous acid is present only if the reaction is too violent. For the detection of the hypochlorous acid the chlorine water is shaken up with an excess of metallic mercury. If hypochlorous acid is present there is formed along with mercurous chloride a soluble oxychloride which is detected in the filtrate by means of sulphuretted hydrogen.

Recovery of Silver Residues.—R. Dietel (*Pharm. Zeitung*).—Already inserted.

Simultaneous Precipitation of Copper and Antimony by the Galvanic Current.—W. Hampe (*Chem. Zeit.*).—This paper will be inserted in full.

Detection and Determination of Arsenic.—Joh. Thiele (*Liebig's Annalen*).—This memoir will be inserted in full.

Detection of Small Quantities of Tartaric Acid and Citric Acid.—L. Crisiner (*Bull. Soc. Chim.*).—The author shows the different behaviour of the two acids with ammonium molybdate in presence of hydrogen peroxide. Citric acid gives no colour, but tartaric acid, even in very small quantities, produces a blue colouration. If we mix 1 grm. pulverised citric acid with 1 c.c. 20 per cent solution of molybdic acid, add from 2 to 3 drops of pure dilute hydrogen peroxide ($\frac{1}{4}$ to 1.5th per cent H_2O_2), and heat for three minutes on the water-bath with repeated agitation, we obtain in the absence of tartaric acid a pure yellow colour, whilst in presence of 2 m.grms. tartaric acid there appears a very distinct blue colour which is perceptible even with 1 m.grm.

Determination of Carbon in Organic Substances in the Moist Way.—K. Okada (*Archiv. f. Hygiene*).—This paper will be inserted as early as possible.

A Source of Error in the Ultimate Analysis of Organic Substances.—G. Neumann.—Ignited copper turnings are capable of absorbing or combining with hydrogen and carbon dioxide. The view of Thudichum, Hake, and Vortmann, that carbon dioxide is capable of expelling hydrogen, was not confirmed. If copper spirals are reduced in methyl- or ethyl-alcohol, an absorption also takes place.

A Modification of the Dumas Process for the Determination of Nitrogen.—F. Blau (*Monatshefte für Chemie*).—This memoir requires the two accompanying figures.

Oxygen in Unroasted Ores.—W. Hampe (*Chemiker Zeit.*).—The author has analysed many lead and copper ores from the Upper Harz, and found in them oxygen which would not have been expected in such unroasted stones. For determining the oxygen 5 grms. of the stone finely powdered and dried at 100° were placed in a weighed bulb-tube of sparingly fusible glass, and then cautiously heated in a current of dry carbon dioxide in order to remove every trace of moisture. After weighing, pure dry oxygen is passed through the tube, and the bulb is heated for a long time to redness, when water escapes. When the reduction is completed, the tube cooled, and the hydrogen expelled by air, it was weighed again. As on reduction in a current of hydrogen, a little sulphur is always carried away as hydrogen sulphide, the tube, during the experiment, is always connected with a vessel containing an alkaline solution of lead. The lead sulphide formed is filtered off and converted into lead sulphate. From the weight of the latter the sulphur is calculated. The loss of weight of the tube, *minus* the weight of the sulphur escaped as sulphuretted hydrogen, gave the weight of the oxygen.

Reaction of Nitrogenous Organic Substances.—H. Aufschläger (*Monatshefte für Chemie*).—This communication chiefly concerns the amides of carbonic acid, uric acid, and their derivatives, the albumenoids, &c. If such compounds are mixed with zinc-powder and heated in a combustion-tube, there is formed among other products zinc cyanide, $Zn(CN)_2$, permanent in heat, the cyanogen in which can be recognised in the usual manner. This reaction is not analogous to the formation of cyanogen on heating nitrogenous organic compounds with potassium, since, unlike the latter, it is not common to all organic compounds. For a qualitative recognition the solid compounds are mixed with zinc-powder and heated in the tube to incipient redness. Liquids are passed in the form of vapour over the metallic compound at incipient redness. When cold the zinc-powder is extracted with soda-lye and tested in the usual manner for cyanogen with ferric chloride and ferrous sulphate and subsequent addition of hydrochloric acid. Quantitative experiments showed that in the mean 50 per cent of the nitrogen present are obtained in the state of cyanogen.

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Medical, 8.30.
 ——— Chemical, 8. (Extra Meeting). "Kopp Memorial Lecture," by Prof. T. E. Thorpe, F.R.S.
 ——— Society of Arts, 8. "The Practical Measurement of Alternating Electrical Currents," by Prof. J. A. Fleming, F.R.S. (Cantor Lectures).
- TUESDAY, 21st.—Institute of Civil Engineers, 8.
 ——— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
 ——— Pathological, 8.30.
 ——— Society of Arts, 3. "Wall-Papers and Stencilling," by T. R. Spence.
- WEDNESDAY, 22nd.—Society of Arts, 8. "Old Age Pensions," by T. Mackay.
 ——— British Astronomical Association, 5.
 ——— Geological, 8.
- THURSDAY, 23rd.—Royal, 4.30.
 ——— Royal Society Club, 6.30.
 ——— Royal Institution, 3. "The Factors of Organic Evolution," by Prof. Patrick Geddes.
 ——— Institute of Electrical Engineers, 8.
- FRIDAY, 24th.—Royal Institution, 9. "Electrical Railways," by Dr. Edward Hopkinson, M.A.
 ——— Physical, 5. "A Handy Folometer," by Prof. J. D. Everett, F.R.S. "Plane and Spherical Sound Waves," by Dr. C. V. Burton. "Motion of a Perforated Solid in a Fluid," by G. H. Bryan, M.A.
- SATURDAY, 25th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1735.

NOTE ON THE SUPERSATURATION OF SOLUTIONS OF OXYGEN IN WATER.

By C. A. SEYLER, B.Sc.

THE determination of free oxygen in water is of interest and importance; but as much time must frequently elapse between the drawing of the sample and the analysis, there is often a considerable rise in temperature before it reaches the analyst. One is therefore troubled by the doubt as to whether the rise of temperature has caused a loss in the oxygen dissolved. Having frequently noticed that the dissolved oxygen is much higher than corresponds to saturation at the temperature of the water on arrival, I made some experiments to test the point. A recent paper by A. H. Gill (*Four. Anal. App. Chem.*, vi., No. 11) induces me to contribute my experience on this important matter, which fully agrees with his results.

The experiments show that in a sample of water, as usually delivered in Winchester quarts nearly full, a rise of some 10° C. is without noticeable effect on the dissolved oxygen. The gaseous solution remains supersaturated, and only parts with the extra oxygen upon vigorous shaking in half empty Winchesters. The experiments were made by the convenient method of Thresh (*Four. Chem. Soc.*, March, 1890), on the water of the Swansea Supply, which is soft and organically pure.

Series I.

	Temp. ° C.	Oxygen, c.c. per litre.	(Roscoe and Lunt). Saturated at
On arrival	5	9.49	1°, 9.48 c.c.
Raised without shaking to	9.5	9.49	1°, 9.48 "
After shaking at	13	7.26	13°, 7.28 "

Series II.

On arrival	9	—	—
On analysis	13	(a) 8.23 (b) 8.11	7.5°, 8.22 " 8°, 8.13 "
After shaking at	13	7.27	13°, 7.28 "
Again raised to	19	7.17	—
After shaking at	20	6.28	20°, 6.28 "

Series III.

Shaken at	13	(a) 7.38 (b) 7.42	13°, 7.28 " —
Raised to	26.5	7.42	—
Shaken at	26.5	5.62	26.5°, 5.64 "

In each case a stoppered bottle was nearly filled with the water, and the temperature raised 5° or 6° in the first two series, and 13.5° in the last, without loss of oxygen occurring. As a check on the analysis, the water was reduced to saturation by shaking and blowing air through it; in the last two cases both before and after raising the temperature, and determining the oxygen.

The results show the importance of knowing the temperature of the water at the time of taking the sample, but unfortunately, like other important local particulars, it is not always easy to obtain.

Technical Institute, Swansea.

The Atomic Weight of Cadmium.—W. L. Lorimer and E. F. Smith.—The authors have electrolysed potassium cadmium cyanide. The mean result is 112.055. —*Zeit. für Analytische Chemie.*

BEHAVIOUR OF THE GADOLINITE EARTHS WITH POTASSIUM CHROMATE.

By G. KRÜSS and A. LOOSE.

(Continued from p. 76).

AN acid solution of the earthy nitrates was treated with potassa-lye until there appeared a very slight permanent precipitate. The liquid was filtered off so as to ensure the possession of a neutral solution. It gave with K_2CrO_4 a yellow, flocculent precipitate resembling aluminium hydroxide. If it was heated, the precipitation was considerably increased, and the yellow colour of the liquid turned to an intense red, the colour of $K_2Cr_2O_7$. To work up this precipitate it was filtered, the deposit washed and dissolved in hydrochloric acid; the addition of alcohol and the application of heat effected the reduction of the chromic acid. In the green solution the acid was partially neutralised with ammonia, so that the earths could be precipitated by oxalic acid.

The filtrate from the first chromate precipitate was treated twice more in the same manner to ascertain whether potassium chromate acted dissimilarly on different earths; whether this method was altogether suitable for fractionated precipitation. The thought suggested itself that the feeblest bases could be least saturated with so feeble an acid as the chromic, and would therefore be most readily precipitated.

The oxalates obtained from the first chromate precipitation were ignited, but to our surprise the colour of the ignited oxides was brown, and showed a large proportion of didymium. This seemed very striking, since didymia as the strongest base should be the last to fall down. The determination of the equivalent, which for the earths

of the initial material showed $R = 102$, gave for this first

chromate precipitate $R = 115.6$. In the second and third precipitate the colour of the earths became paler again;

we found $R = III$ and $R = 104.3$. Whether the amount of the R obtained as such represented the average earths of the three fractions or was exclusively due to the quantity of didymia present, we may learn by a consideration of the spectra:—

First Fraction.

λ .	Strength of absorption.	Symbol.
728.3.. .. .	Very strong	Dia
679.4.. .. .	Distinct	Di β
654.7.. .. .	Trace	Era
640.4.. .. .	"	Xa
579.2.. .. .	Extremely strong	Di γ
523.1.. .. .	Very strong	Er β
512.2.. .. .	Distinct	Di ϵ
482	"	Di ζ
477.7.. .. .	"	Sm β
469	"	Di η
463.2.. .. .	"	Sm β
445.1.. .. .	Very strong	Di δ
452.6.. .. .	Faint	X ζ
536.3.. .. .	Very faint	X γ
428.5.. .. .	Rather distinct	X η
409	Rather strong	Sm β

Second Fraction.

728.3.. .. .	Very distinct	Dia
679.4.. .. .	Very faint	Di β
840.4.. .. .	Trace	Xa
579.2.. .. .	Very strong	Di γ
523.1.. .. .	Very distinct	Er β
512.2.. .. .	Faint	Di ϵ
482	"	Di ζ
477.7.. .. .	"	Sm β
469	"	Di η

λ .	Strength of absorption.	Symbol.
463	Faint	Sm β
452'6.. ..	Distinct	X ζ
445'1.. ..	Faint	Di δ

Third Fraction.

728'3.. ..	Distinct	Di α
579'2.. ..	Faint	Di γ
523'1.. ..	Distinct	Er β
512'2.. ..	Faint	Di ϵ
445'1.. ..	Very faint	Di δ

As it is easy to see in the first fraction, the didymium and erbium oxides, *i.e.*, exactly the strongest and the weakest of the bases occurring in the material, are simultaneously accumulated. Yttrium, with its reducing effect on the atomic weight, appears only in the following fractions. This remarkable fact leads to the following considerations.

The red colour of the solution observed on heating is evidently due to the formation of acid potassium chromate. This may take place either, as it was supposed, by a part of the salts losing chromic acid and being converted into a basic salt or hydroxide; two cases are here probable:—

1. Only the feeble bases are decomposed; the decomposition then ensues in the inverse proportion of the basicity.

2. All the bases are simultaneously decomposed. Against the latter assumption it must be considered that yttrium appears only in the latter of the above named fractions.

In favour of the second case it must be considered that in the first fraction didymium and erbium were precipitated together. But the possibility must not be overlooked that Di might be precipitated as a sparingly soluble salt, whilst the more feebly basic Er was thrown down as a basic compound.

On this point we could only reach certainty by sometimes increasing the decomposition of earthy salts and sometimes reduced to a minimum by the application of different temperatures. The portions precipitated in the cold were therefore examined separately from those deposited on heating.

A fresh portion of the same material ($R=102$) was mixed with potassium chromate, with careful refrigeration, as long as a perceptible increase of the precipitate was observed. The precipitate was filtered off, the yellow filtrate heated, and the solution thus strongly reddened was separated from the precipitate formed. The filtrate of this second precipitate thrown down in heat was then treated twice in the same manner, forming thus three fractions, each of which is divisible into a portion precipitated in the cold, and one thrown down in heat.

From the equivalents of the earths as found, we calculated the following values for R in the single fractions, the absorption spectra of which are appended.

First Fraction.

A.—Precipitated in the Cold, $R=120'9$.

λ .	Strength of absorption.	Symbol.
728'3.. ..	Very strong	Di α
679'4.. ..	Distinct	Di β
579'2.. ..	Extremely strong	Di γ
523'1.. ..	Very strong	Er β
512'2.. ..	Fading	Di ϵ
482	Distinct	Di ζ
477'7.. ..	"	Sm β
469	"	Di η
463'2.. ..	"	Sm β
445'1.. ..	Extremely strong	Di δ
428'5.. ..	Very strong	X η
409	Broad, fading	Sm β

B.—Precipitated in Heat, $R=111'7$.

λ .	Strength of absorption.	Symbol.
728'3.. ..	Strong	Di α
679'4.. ..	Faint	Di β
579'2.. ..	Strong	Di γ
523'1.. ..	"	Er β
512'2.. ..	Faint	Di ϵ
445'1.. ..	Rather strong	Di δ
452'6.. ..	Very distinct	X ζ

Second Fraction.

A.—Precipitated in the Cold, $R=113$.

728'3.. ..	Strong	Di α
679'4.. ..	"	Di β
579'2.. ..	"	Di γ
523'1.. ..	"	Er β
512'2.. ..	Faint	Di ϵ
482	Strong	Di ζ
477'7.. ..	"	Sm β
469	"	Di η
463'2.. ..	"	Sm β
445'1.. ..	Very strong	Di δ

B.—Precipitated in Heat, $R=107$.

728'3.. ..	Strong	Di α
679'4.. ..	Distinct	Di β
654'7.. ..	"	Er α
640'4.. ..	"	X α
579'2.. ..	Strong	Di γ
536'3.. ..	Thin and sharp	X γ
531'3.. ..	Very faint	Di
523'1.. ..	Very strong	Er β
512'2.. ..	Fading	Di ϵ
482	Distinct	Di ζ
477'7.. ..	"	Sm β
469	"	Di η
463'2.. ..	"	Sm β
452'6.. ..	Very distinct	X ζ
445'1.. ..	Very strong	Di δ
428'5.. ..	Distinct	X η

Third Fraction.

A.—Precipitated in the Cold, $R=107'6$.

728'3.. ..	Very strong	Di α
708	Very faint	Di
679'4.. ..	Faint	Di β
579'2.. ..	Very strong	Di γ
523'1.. ..	Strong	Er β
512'2.. ..	Fading	Di ϵ
482	Rather strong	Di ζ
477'7.. ..	"	Sm β
469	"	Di η
463'2.. ..	"	Sm β
445'1.. ..	Very strong	Di δ
428'5.. ..	Trace	X η

B.—Precipitated in Heat, $R=102'4$.

728'3.. ..	Strong	Di α
679'4.. ..	Faint	Di β
654'7.. ..	Distinct	Er α
579'2.. ..	Strong	Di γ
523'1.. ..	{ Very strong and sharp }	Er β
512'2.. ..	Fading	Di ϵ
482	Very faint	Di ζ
477'7.. ..	"	Sm β
469	Distinct	Di η
463'2.. ..	Very faint	Sm β
445'1.. ..	Rather strong	Di δ

Residue : $R=99'8$.

λ .	Strength of absorption.	Symbol.
728'3.. ..	Rather strong	Di α
679'4.. ..	Very faint	Di β
654'7.. ..	"	Er α
579'2.. ..	Rather strong	Di γ
523'1.. ..	"	Er β
512'2.. ..	Faint	Di ϵ
482	Very faint	Di ζ
477'7.. ..	"	Sm β
469	"	Di η
463'2.. ..	"	Sm β
445'1.. ..	Rather strong	Di δ

It will be seen from these tables that didymium is chiefly concentrated in the cold precipitations, whilst the hot precipitations contain relatively more erbium.* As the same time, the determinations of the equivalents of the elements precipitable in heat give always smaller combining weights than the cold precipitations,—a sign

III
that yttria (Y=89—90) was thrown down to a small extent in the cold precipitations but in larger quantities in the precipitations given by potassium chromate in heat. Yttria, according to spectroscopic observations, is chiefly accompanied by the more feebly basic erbia. The new separation on heating solutions precipitated with K₂CrO₄ is, in fact, a consequence of the feeble basicity of these earths, and considered in conjunction with the red colouration of the solutions,—a sign of the decomposition.

Potassium chromate, therefore, acts upon the nitrate solution of the rare earths in a twofold manner: in cold chiefly as a precipitant for didymium chromate, but in heat as an agent for the separation of the basic erbium and didymium compounds. These distinctions are far remote from being utilised for the quantitative separation of these earths. We possess, indeed, hitherto no even approximately accurate method for the quantitative separation of the oxides of this group. Still, neutral potassium chromate is perhaps peculiarly applicable in working up rare earths, since by alternating precipitation in cold and heat we may separate alternately from a mixture of these oxides the stronger and then again the weaker bases, and thus attack the earths to be separated from two different sides.

(To be continued).

MANURIAL EXPERIMENTS WITH TURNIPS.†

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(Concluded from p. 68).

THE last series of experiments were those carried out by Mr. James Fulton on his farm at Balshagray, Whiteinch, near Glasgow.

The experimental plots were situated in the centre of a large field with a fair southern exposure, and on perfectly level ground. The soil is described by Mr. Fulton as "a good loam with a touch of clay in it."

The past history of the field since 1885 is as follows:—

1885. Turnips, which received 40 tons farmyard manure to the acre.

1886. Wheat, which received no manure.

1887. Hay, which received nitrate of soda.

1888. Potatoes, which received 15 tons farmyard manure and 3 cwt. special artificial potato manure.

The plots were eleven in number, and consisted each of 1-20th of an acre in extent; each plot being three

yards wide—containing four drills—and running from north to south.

The manures used in these experiments consisted of slag, superphosphate, and farmyard manure. Owing to a mistake, nitrate of soda was forgotten to be applied. The variety of turnip used in this case was the Purple Top Swede. The manures and the turnips were sown on the 22nd of May. There was no rain for five days after sowing. They were thinned on the 21st of June, and lifted on the 19th of November.

The following Table exhibits the quantities of manures and returns of turnips yielded by the different plots:—

No.	Manure.	Produce.		Increase over nothing plots.	
		Tons.	cwt.	Tons.	cwt.
1.	Nothing	16	—	—	—
2.	6 cwt. slag	17	5	1	5
3.	2½ cwt. super	16	10	—	10
4.	12 cwt. slag	18	—	2	—
5.	5 cwt. super	17	15	1	15
6.	4 cwt. slag and 10 tons dung	20	10	4	10
7.	4 cwt. slag and 10 tons dung	20	10	4	10
8.	6 cwt. slag and 10 tons dung	20	—	4	—
9.	6 cwt. slag and 10 tons dung	20	10	4	10

The largest increase will be seen in plot No. 9, receiving 6 cwt. slag; but between this plot and plots Nos. 6 and 7—receiving 4 cwt. of slag and 10 tons dung—there is practically very little difference.

The largest increase is in plots Nos. 5 to 9, receiving different quantities of slag along with 10 tons of dung, the plots receiving the smaller quantity of slag showing an equal increase to those receiving the larger quantity of slag. With regard to the plots receiving slag and super alone, it will be seen that in both cases the slag gives distinctly better results than the super. The following Table exhibits the cost of the manures and the value of the increase. The turnips were sold at 16s. per ton:—

No.	Manure.	Cost.	Value of increase in crop.	
			£	s
2.	6 cwt. slag	£0 6 0	£0	19 6
3.	2½ cwt. super	0 6 10	0	8 0
4.	12 cwt. slag	0 12 0	1	12 0
5.	5 cwt. super	0 13 8	1	8 0
6.	4 cwt. slag and 10 tons dung	3 4 0	3	12 0
7.	4 cwt. slag and 10 tons dung	3 4 0	3	12 0
8.	6 cwt. slag and 10 tons dung	3 6 0	3	4 0
9.	6 cwt. slag and 10 tons dung	3 6 0	3	12 0

These figures show again that the most profitable manure is the slag; and that the farmyard manure, even applied at the rate of 10 tons an acre, did not pay.

N.B.—The following Table contains the results of all the experiments in a convenient form.

The following conclusions may be drawn from the results of these experiments:—

1. That while farmyard manure is valuable in giving the crop a good start and bringing it well forward during the period of germination and early growth by supplying a certain amount of easily assimilable plant food, and, in the case of dry weather, attracting a quantity of moisture, it is not profitable—as far as first year's results are concerned—when applied in such quantities as 20 or even 10 tons per acre.

2. That the basic slag proved by far the most economical of the manures used; and that, further, the

* The X lines, excepting X_η, likewise appear chiefly in the hot precipitations, as may be seen from the second fraction (B).

† From the Transactions of the Highland and Agricultural Society of Scotland.

Manures.		Tons. cwt.	Cost.			Increase in crops over nothing plots.			Value of increase.			Profit.			Value of increase due to dung.			Cost of dung.			Value of increase due to nitrate.			Cost of nitrate.		
			£	s.	d.	Tns. cwt. qr.	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.		
Slag	..	0 6	0	6	0	2 8	0	1 9	0	1 3	0	—	—	—	—	—	—	—	—	—	—	—	—			
"	..	0 6	0	6	0	8 19	0	4 13	0	4 7	0	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 6	0	6	0	1 5	0	0 19	6	0 13	6	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 12	0	12	0	9 14	0	3 17	6	3 5	6	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 12	0	12	0	7 0	0	4 4	0	3 12	0	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 12	0	12	0	2 0	0	1 12	0	1 0	0	—	—	—	—	—	—	—	—	—	—	—				
Super	..	0 2½	0	6	10	0 10	0	0 8	0	0 1	2	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 4	0	11	0	4 5	0	2 11	0	2 0	0	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 4	0	11	0	10 17	3	4 6	0	3 15	0	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 8	0	13	8	1 15	0	1 8	0	0 14	4	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 8	1	2	0	6 8	0	3 17	0	2 15	0	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 8	1	2	0	11 12	0	4 13	0	3 11	0	—	—	—	—	—	—	—	—	—	—	—				
"	..	0 9	1	5	0	3 18	0	2 15	0	1 10	0	—	—	—	—	—	—	—	—	—	—	—				
Slag	..	0 6	4	16	0	16 10	1	6 12	0	1 16	0	1 19	0	4 10	0	—	—	—	—	—	—	—				
Dung	..	15 0								(loss)																
Slag	..	0 6	3	6	0	4 0	0	3 4	0	0 2	0	2 4	6	3 0	0	—	—	—	—	—	—	—				
Dung	..	10 0								(gain)																
Slag	..	0 6	3	6	0	4 10	0	3 12	0	0 6	0	2 12	6	3 0	0	—	—	—	—	—	—	—				
Dung	..	10 0																								
Slag	..	0 4	3	4	0	4 10	0	3 12	0	0 8	0	2 19	0	3 0	0	—	—	—	—	—	—	—				
Dung	..	10 0																								
Slag	..	0 4	3	4	0	4 10	0	3 12	0	0 8	0	2 19	0	3 0	0	—	—	—	—	—	—	—				
Dung	..	10 0																								
Slag	..	0 6	6	6	0	9 3	0	5 10	0	(loss)																
Dung	..	20 0								0 16	0	4 1	0	6 0	0	—	—	—	—	—	—	—	—	—	—	—
Slag	..	0 12	6	12	0	11 15	0	7 1	0	(gain)																
Dung	..	20 0								0 9	0	5 12	0	6 0	0	—	—	—	—	—	—	—	—	—	—	—
Slag	..	0 12	5	2	0	17 16	2	7 2	8	2 0	8	3 5	2	4 10	0	—	—	—	—	—	—	—				
Dung	..	15 0																								
Slag	..	0 14	6	14	0	7 18	0	5 11	0	(loss)																
Dung	..	20 0								1 3	0	0 11	0	6 0	0	—	—	—	—	—	—	—	—	—	—	—
Super	..	0 5	6	13	9	16 8	0	9 17	0	(gain)																
Dung	..	20 0								3 3	3	8 9	0	6 0	0	—	—	—	—	—	—	—	—	—	—	—
Super	..	0 7	6	19	0	7 13	0	5 6	0	(loss)																
Dung	..	20 0								1 13	0	3 3	3	6 0	0	4 6	0	0 10	0	—	—	—	—	—	—	—
Slag	..	0 7	6	17	0	10 3	0	7 2	0	(gain)																
Dung	..	20 0								0 5	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Nitrate..	0 1																									
Slag	..	0 14	7	4	0	11 3	0	7 16	0	0 12	0	—	—	—	—	—	—	—	—	—	—	—				
Dung	..	20 0																								
Nitrate..	0 1																									
Slag	..	0 6	5	6	0	19 17	3	7 19	0	2 13	0	—	—	—	—	—	—	—	—	—	—	—				
Dung	..	15 0																								
Nitrate..	0 1																									
Slag	..	0 12	5	12	0	20 0	1	8 0	0	2 8	0	—	—	—	—	—	—	—	—	—	—	—				
Dung	..	15 0																								
Nitrate..	0 1																									
Slag	..	0 6	6	16	0	13 18	0	8 1	0	1 5	0	—	—	—	—	—	—	—	—	—	—	—				
Dung	..	20 0																								
Nitrate..	0 1																									
Slag	..	0 12	7	2	0	14 8	0	8 13	0	1 11	0	—	—	—	—	—	—	—	—	—	—	—				
Dung	..	20 0																								
Nitrate..	0 1																									

larger quantities of slag proved more profitable than the smaller.

3. That superphosphate of lime was also a profitable manure, and that, as in the case of the slag, the larger quantities gave better results than the smaller.

4. That nitrate of soda in every case showed itself to be a most profitable manure.

The Determination of Sulphur in Combustibles by the Eschka Process.—This method has been discussed in the "Bulletin of the Engineers' Society of Western Pennsylvania." According to Mr. Jas. Handy the Eschka process furnishes identical results both in its original form and in the modification introduced by Dr. Hundeshagen, which latter presents no advantages. Another chemist present, Mr. Jas. Camp, confirmed the results of Mr. Handy.—*Rev. Univ. des Mines*, xx, No. 2.

ON THE GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 78).

Effect of Vitrioled Pumice on Hydrogen Gas.

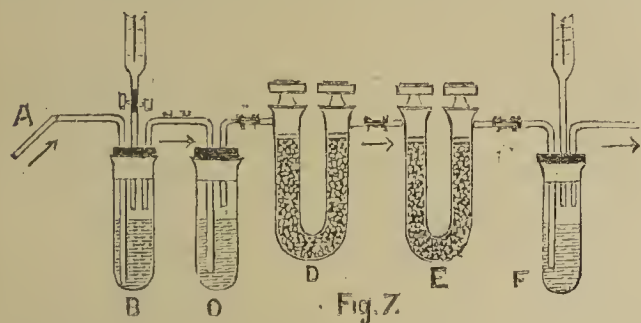
To form an idea of the extent to which Dumas's syntheses may have been vitiated by the formation of sulphurous acid in the vitrioled pumice tubes which he used for drying his hydrogen, we produced a continuous current of Dumas's hydrogen and determined the volume of a standard solution of permanganate which a given volume of the gas decolorised.

As a necessary preliminary, a current of hydrogen,

* *Proceedings of the Philosophical Society of Glasgow.*

which had been purified only by passing it through the acetate of lead, the nitrate of silver, and the caustic potash tubes of the Dumas's set, was sent through a quantity of acidulated water which had been just barely reddened by addition of a drop of permanganate. After the gas had been going through for four hours, the reagent had turned brownish through partial reduction of the Mn_2O_7 to MnO_2 ; hence it was proved that pure hydrogen does not act sufficiently on permanganate to prohibit the projected method of analysis.

This point being settled, the two long vitriol tubes were appended to the Dumas's set, the hydrogen turned on, and kept going until all the air was sure to be expelled. The following set of successive apparatus (see Fig. 7) was



then appended to the outlet of the last vitriol tube:—A test-tube, B, containing some water and dilute sulphuric acid; a similar test-tube, C, charged with alkaline permanganate; two small successive U-tubes, D and E, charged, the first with fragments of caustic potash, the second with vitrioled pumice; and lastly, a test-tube, F, similar to B and C. The test-tubes B and F both communicated with a burette containing standard permanganate. From the outlet of F the gas passed into a graduated Pisani bottle to be measured there. The apparatus being adjusted, hydrogen was passed through it, and the sulphurous acid contained in the gas titrated as it came by occasional addition of permanganate from out of the burette so as to maintain a distinct red colouration in the respective liquids. The maintenance of the end reaction, however, became more and more difficult as the experiment progressed, on account of the formation of precipitates of MnO_2 in the reagents.

In all, 12 litres of gas were passed through the apparatus, and, as far as we were able to determine the SO_2 , it amounted to 4.8 m.grms. in test-tube B, and to 0.48 m.grm. in F. These numbers of course could be looked upon only as rough approximations.

Hence, in a *Second Experiment*, the sulphurous acid in the gas was determined more exactly by passing it through 8 c.c. and 4 c.c. of permanganate (1 c.c. = 5.572 m.grm. of iron) contained in two successive Erlenmeyer flasks, B and C (substituted for the test-tubes previously used), besides some sulphuric acid, and determining the SO_2 absorbed at the end of the experiment by adding a known excessive weight of standardised ferrous sulphate and titrating back with the permanganate. The tube F received 0.3 c.c. of permanganate, which were just decolorised by the 10 litres of gas which passed through the apparatus in three hours. The SO_2 absorbed in B and C amounted to 11.89 m.grms., or to 1.19 m.grm. per litre. Before this experiment was started the Dumas's set of purifying tubes, including the two terminal vitriol tubes, had been standing filled with hydrogen for two days.

Hence, in a *Third Experiment*, those two tubes were emptied out, and the vitrioled pumice fragments evaporated to dryness in a platinum basin; fresh vitriol was then poured on them, and the greater part of this again was chased away by evaporation. The pieces of pumice were then lifted out by means of a platinum forceps, replaced in their tubes, and the experiment then started without unnecessary delay. The residual vitriol in the basin was tested for sulphurous acid and found pure. In 3.5 hours 18 litres of hydrogen were passed through. The

SO_2 formed amounted to 16.4 m.grms., or to 0.91 m.grm. per litre of gas.

Dumas's syntheses, as we are told, often took over twelve hours for their completion; hence, in all those cases in which vitriol was used as a dehydrating agent, the hydrogen must have been contaminated with sulphurous acid. For every 2 m.grms. of SO_2 which passed over Dumas's red-hot oxide of copper, the residual copper contained 1 m.grm. of sulphur as Cu_2S , and the water collected included 1.125 m.grm. of water produced from the oxygen of the sulphurous acid. Supposing the loss of weight suffered by the reduction tube amounted to S, and the weight of SO_2 acting upon the oxide of copper was = n, the oxygen which produced the W parts of

water obtained amounted to $S + \frac{n}{2} + \frac{n}{2} = S + n$ parts.

Hence we have for the true value k_0 of the ratio $H_2O : O$,

$$k_0 = \frac{W}{S + n} = \left(\frac{W}{S} = k \right) \times \frac{1}{1 + n/S}.$$

For a guess at the correcting factor, let us take $S = 8000$ m.grms., and assume that the hydrogen used for the conversion of that oxygen into water amounted to 12 litres; whence $n = 12 \times 0.91$ by Experiment III. Hence

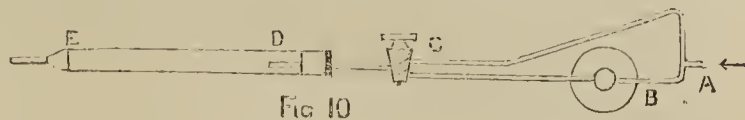
$1 : (1 + \frac{n}{S}) = 1 - 0.001365$. Now, according to our cal-

culation, Dumas's value for k , uncorrected for adventitious oxygen, was = 1.12547; hence we have by the formula, $k_0 = 1.12393$, and for $H_2 : O$ the number 0.12393.

Those of Dumas's syntheses, in which phosphoric anhydride was used instead of oil of vitriol, ought to be free of the sulphurous acid error, but we do not find any confirmation of this in his tabular statement of results; hence we presume that the phosphoric anhydride was used only as an auxiliary to oil of vitriol.

Some time after these experiments had been made, it struck us that we had better make sure of our theory of the effect of the sulphurous acid in the hydrogen on the results of a synthesis of water. After some pioneering work, the following method was adopted and carried out:—

A combustion-tube, charged with pure reduced copper, was made to communicate, by its outlet end (indirectly *vide infra*), with a graduated Pisani bottle, and by its inlet end with a two-way glass stopcock communicating with a Kipp (charged with zinc and dilute sulphuric acid) in such a manner that we were able to let the hydrogen go by either of two prescribed ways (see Fig. 10). The



hydrogen was purified by passing it, first through a large tower filled with pieces of caustic soda, and then through a tube full of red-hot copper gauze. If the gas went one way, it entered the combustion tube containing the reduced copper as it was; if it went the other way, it had to pass through a two-litre bottle, B, which was almost completely filled with a solution of sulphurous acid. A special experiment showed that the gas, as it came out of the sulphurous acid bottle, contained 3.16 m.grms. of SO_2 per litre.

In the experiment, the first step was to pass pure hydrogen over the red-hot reduced copper. A test-tube containing a quantity of acidulated water, coloured just perceptibly with permanganate, was then inserted between the outlet end of the reduced copper tube and the Pisani bottle, and seven litres of hydrogen, contaminated with SO_2 were passed through. The permanganate retained its colour, showing that no SO_2 got past the red-hot copper. In a subsequent experiment, the combustion tube was filled with oxide of copper, and an apparatus for

the collection of the water formed inserted between the oxide of copper tube and the test-tube. As in the former case the reduction was started with pure hydrogen, impure hydrogen was then made to go through, and pure hydrogen again substituted for it at the end. About 50 grms. of oxide of copper were used, corresponding to 10 litres of hydrogen. The permanganate in the test-tube retained its colour, and the water collected as such was found free of sulphurous acid. This shows that neither copper nor oxide of copper allows any sulphurous acid to pass, or, in other words, that the sulphurous acid is decomposed completely with formation of sulphide of copper.

(To be continued).

JEAN SERVAIS STAS.

It is a year since Science lost one of its most eminent representatives in the person of Jean Servais Stas. Six months before his death, when the Academy of Belgium celebrated the rare anniversary of fifty years of assiduous participation in his researches,—fifty years filled with the most persevering industry, the most remarkable discoveries,—Europe and America joined in hailing this great genius, this powerful and laborious investigator.

The researches of Stas on the atomic weights, on the laws of chemical proportions, on nicotine and the organic alkalies, on the constitution of matter, and on solar light, have placed him from the outset of his career and kept him up to its conclusion in the first rank among the masters of modern chemistry. As a superior analyst his works are of fundamental importance, and have supplied chemistry with foundations which cannot be shaken. By the extent of his researches, the profundity of his insight, the accuracy and the novelty of his methods, the works of Stas have become classical, and his name is inseparable from the very principles of Science.

This is not the limit of his fruitful influence. As Professor for twenty-five years at the Military School he has exercised a durable influence by his example and his advice. As a Commissioner of the Mint from 1865 to 1872 he brought this delicate function into exceptional prominence by the moral authority which in him was combined with the scientific spirit in so high a degree. The services which he rendered to the superior Sanitary Council, to the Central Statistical Commission, to University education, to the State Agricultural Laboratories, to the National Bank, and to various important branches of industry are not forgotten. At the Conference on the Metre and at the International Committees of Weights and Measures the activity of Stas was not less important, and the conclusions of his prolonged researches are now part and parcel of public law in most civilised nations.

It would be superfluous to insist on his great and manifold merits; they have been admitted at their full value by the unanimous testimony of the most eminent *savants* of our epoch.

The man, we must remember, was always on a level with his work. Nobility of soul, firmness of convictions, disinterestedness carried to the length of self-sacrifice, extreme simplicity of life, affectionate devotion to his friends, his colleagues, his pupils, to everyone who sought his advice or his support,—these were the universally known features of the moral character of Stas.

The memory of such a man cannot be too much honoured. The true monument is his works. Unfortunately, copies of the works of Stas have become scarce. The first duty which his friends and admirers seek to fulfil towards him is to secure the perpetuity of his works by a wide circulation. A new edition, grouping his memoirs, notes, and reports, scattered in fifty volumes, and reproducing them in a more convenient form, is a necessary enterprise.

A commemorative monument will complete this homage, and will recall a life entirely devoted to Science and to the public good.

In order to accumulate the resources—relatively considerable—which will be necessary to raise such a monument, and to re-edit the works of Stas, we make a warm appeal for the assistance of all who are interested in the progress of Science and of mankind.

Adhesions and subscriptions will be received by M. L. Errera, 1, Place Stephanie, Brussels.

List of Members of the Committee.—L. Aronstein, Ad. von Baeyer, E. Banning, M. Berthelot, V. Bidez, C. Blas, C. Blomstrand, A. J. Bosmans, A. Brialmont, C. Buls, R. Bunsen, S. Cannizzaro, Fr. W. Clarke, A. Cossa, W. Crookes, J. Delbœuf, J. B. Depaire, Baron de Selys-Longchamps, J. de Tilly, J. Dewar, P. de Wilde, H. C. Dibbitts, E. du Bois-Reymond, E. Dupont, L. Errera, Ch. Faider, H. Faye, Ed. Fétis, E. Fischer, R. Fittig, W. Foerster, F. Folie, C. A. Fraikin, A. Franchimont, G. Frédéricx, M. Frémy, W. Frère-Orban, R. Fresenius, C. Friedel, A. Gilkinet, C. Graebe, Ch. Graux, M. Hagenbach-Bischoff, J. Hall, Dr. P. Héger, H. von Helmholtz, E. Hennequin, P. Henrard, L. Henry, A. Herlant, Ch. Hermite, Ad. Hirsch, Aug. Kekulé, G. Krüss, Baron F. A. Lambermont, H. Landolt, J. Leclerc, A. Lieben, A. Limpricht, G. D. Liveing, Norman Lockyer, G. Lunge, J. Maes, J. W. Mallet, G. de Marignac, G. Matthey, H. Maus, D. Mendeleeff, N. Mentschutkin, Ch. Mesdach de ter Kiele, Lothar Meyer, Victor Meyer, G. Montefiore Levi, G. Morel, Baron A. Nicaise, L. F. Nilson, W. Ostwald, L. Pasteur, W. H. Perkin, A. Petermann, O. Pettersson, Abbé A. Renard, A. Rivier, Dr. W. Rommelaere, Sir H. Roscoe, E. Rousseau, J. Sauveur, Hugo Schiff, M. Schützenberger, E. Solvay, W. Spring, Th. Swarts, Fr. Terby, E. Terssen, C. von Than, William Thomson (Lord Kelvin), G. Tiberghien, M. Troost, J. Tyndall, C. van Bambeke, Ed. van Beneden, P. J. van Beneden, van den Kerchove, Van der Kelen, G. Van der Mensbrugge, J. D. van der Plaats, M. Vandeveld, V. van Hoegaerden, H. Van Neuss, van Riemsdyk, J. H. van't Hoff, A. Vergote, Th. Vincotte, Dr. V. Vleminckx, H. Wauwer-mans.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 19th, 1893.

Prof. A. CRUM BROWN, President, in the Chair.

(Concluded from p. 82).

101. "Salts of Active and Inactive Glyceric Acid; the Influence of Metals on the Specific Rotatory Power of Active Acids." By PERCY F. FRANKLAND, F.R.S., and J. R. APPLEYARD.

The authors have prepared and analysed a number of salts both of ordinary glyceric acid and of the dextro-rotatory variety previously described by P. F. Frankland and Frew (*C. S. Trans.*, 1891, 96); the solubilities of many of them, and also the specific rotatory power in the case of the active salts, have been ascertained. The composition and solubilities of the corresponding salts are contrasted.

The specific rotatory powers of the several salts, determined in solutions containing about 10 per cent, are recorded in the following table, together with the molecular rotations of the salts and the calculated specific rotation of the glyceric acid corresponding to each salt.

The authors point out that the variations in the values for the specific rotation of the glyceric acid according to the different metals present in the salt. These values may be represented in round numbers, as unity in the case of the acid potassium salt, 1.5 in the case of the salts of the alkaline earths, 2 in that of the salts of the alkalis, magnesium, and cadmium, and 3 in the case of

Salt.	Specific rotation, [α] _D .	Molecular rotation, $M \times [\alpha]_D = [M]_D$ 100	Equivalent specific rotation of glyceric acid, C ₃ H ₅ O ₄ .
Li(C ₃ H ₅ O ₄)	-20°66'	-23°14'	-21°83'
Na(C ₃ H ₅ O ₄)	-16°13'	-20°65'	-19°48'
K(C ₃ H ₅ O ₄)	-16°46'	-23°70'	-22°36'
K(C ₃ H ₅ O ₄)(C ₃ H ₆ O ₄)	-9°24'	-23°10'	-10°90'
NH ₄ (C ₃ H ₅ O ₄)	-18°05'	-22°20'	-20°94'
Ca(C ₃ H ₅ O ₄) ₂	-13°34'	-33°35'	-15°73'
Sr(C ₃ H ₅ O ₄) ₂	-11°91'	-35°44'	-16°72'
Ba(C ₃ H ₅ O ₄) ₂	-10°01'	-34°73'	-16°38'
Mg(C ₃ H ₅ O ₄) ₂	-20°08'	-46°99'	-22°16'
Zn(C ₃ H ₅ O ₄) ₂	-23°63'	-65°05'	-30°69'
Cd(C ₃ H ₅ O ₄) ₂	-15°29'	-49°23'	-23°22'

the zinc salt. They compare these results with those which have been obtained by other observers in the case of other active acids and which have led to the generally accepted doctrine that the activity of an acid is influenced by the nature of the metal introduced in forming the salt. This doctrine is founded on the observations of Hoppe-Seyler on cholalic acid, of Oudemans on podocarpic and quinic acids, of Hartmann on camphoric acid, and of Landolt on tartaric acid. The authors, however, call attention to the fundamental optical difference between most of these acids and glyceric acid: thus the rotation of the glycerates is both opposite in sign and much greater in degree than that of the acid, whilst, on the contrary, cholalic and camphoric acids have a greater rotation than may be deduced from their salts; and podocarpic acid again has practically the same rotation as may be calculated from its salts. Quinic acid, however, has a somewhat higher rotation than that deducible from its salts, and the same relationships between the rotations of the quinates subsist in miniature as are exhibited on an exaggerated scale by the glycerates; zinc quinate having a distinctly higher, and barium quinate a distinctly lower, rotation than that of the other quinates. In the case of tartaric acid, again, a much higher rotation may be deduced from its salts than is shown by the acid, but the salts of tartaric acid which have been examined for rotation are just those in which only comparatively insignificant differences are observable in the case of the glycerates, viz., the salts of the alkaline metals and magnesium; on the other hand, the excessively high rotation of tartar emetic shows that the antimonyl group, at any rate, has a most important influence in affecting the rotation of the acid. In the case of lactic acid, however, there is the fullest analogy to glyceric acid, the rotation of the lactates being both opposite in sign and much greater in degree than that of the acid, the ratio of the rotation in the zinc salt to that in the calcium salt (the only two lactates which have had their rotation determined) being also almost identical for lactic and glyceric acid, being 1·805 and 1·951 respectively.

Before drawing any conclusions from these remarkable apparent relationships, the authors intend making a more detailed investigation of the rotations of these and other salts in solutions of different concentration. The results, however, as far as they go, appear to lend support and to extend the views on multiple rotation which have been expressed by Mulder (*Chem. Zeit.*, 1868, 58), Krecke (*J. Pr. Chem.*, v., 1872, 6), Landolt (*Ber.*, vi., 1873, 1073), and M. Thomsen (*Ber.*, 1880, 2168, 2264, 2269; 1881, 29, 134, 203, 807, 1647), but subsequently controverted by Landolt (*Ber.*, 1881, 296, 1048) and Oudemans (*Rec. Trav. Chim.*, 1885).

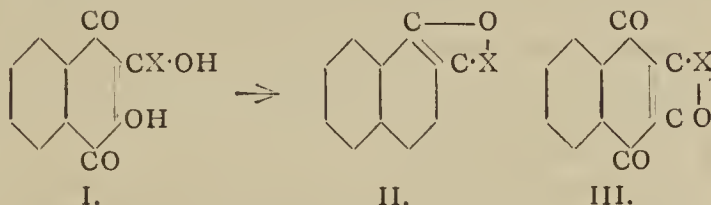
102. "Dibromo-β-lapachone." By SAMUEL C. HOOKER and A. D. GRAY.

Dibromo-β-lapachone was first obtained in very small quantity as a secondary product in the preparation of bromo-β-lapachone (*cf. Trans.*, 1892, 640); although it was formed in the preparation of bromo β-lapachone from lapachol, it was, nevertheless, impossible to produce it

from bromine and pure bromo-β-lapachone. It is now shown that hydrogen bromide plays an important part in the conversion of the mono- into the di-bromo-derivative, an unstable additive compound of the former with bromine and hydrogen bromide being produced, which slowly passes into dibromo-β-lapachone. A number of derivatives prepared from dibromo-β-lapachone are described.

103. "The Conversion of Para- into Ortho-quinone Derivatives." By SAMUEL C. HOOKER.

The author announces that he will subsequently adduce experimental evidence showing that, both in the lapachol and other groups, compounds derived from α-naphthaquinone, of the type represented by formula I., are far more readily converted by the action of acids into anhydrides derived from β-naphthaquinone (II.) than, as might, perhaps, have been expected, into anhydrides of the α-quinone type (III.).



Thus, the benzal-dis-hydroxy-α-naphthaquinone of Zincke and Thelen (*Ber.*, xxi., 2203) is quantitatively converted into an anhydride derived from the β-quinone. A variety of similar compounds, derived from aldehyds other than benzaldehyds, have been prepared.

It will also be shown that, as in the case of the β-lapachones, the converse change of β-quinone anhydrides into α-quinone derivatives is easily effected by boiling with dilute solutions of caustic alkali. It is proposed to extend the experiments to hydroxyquinones generally.

104. "The Nitro derivatives of Phenolphthalein." By JOHN A. HALL, M.Sc.

The author calls attention to the previous incidental references to nitro-derivatives of phenolphthalein by Baeyer (*Annalen*, ccii., 73), Frande (*Ibid.*, p. 154), and O. Fischer (*Ibid.*, ccvi., 99).

As a pure dinitro-derivative was not obtained by nitrating a sulphuric acid solution, phenolphthalein was dissolved in ten times its weight of acetic acid; a mixture of nitric acid and acetic acid was slowly added to the solution, keeping the temperature below 10°; 2 mols. of nitric acid were required by each mol. of phenolphthalein. After a time, a considerable quantity of yellow needles separated, which, after repeated re-crystallisations, melted constantly at 196°. A nitrogen determination gave 6·91 per cent; that calculated for dinitrophenolphthalein, C₁₀H₁₂O₈N₂, is 6·86 per cent.

Dinitrophenolphthalein forms yellow needles, fairly soluble in acetic acid and alcohol; it dissolves in alkalis with a yellow colour, but has practically no affinity for animal fibres. On reduction with sodium sulphide, it yields a fine blue solution, which, however, is very un-

stable. Frande states that, on reduction, his dinitro-cresolphthalein yielded a blue solution, from which he isolated an amido-compound, but apparently did not analyse it. Some attempts were made to condense phthalic anhydride, and ortho- or para-nitrophenol, but without success.

Tetranitrophenolphthalein.—Phenolphthalein dissolved in five times its weight of sulphuric acid was nitrated with 2 mol. proportions of nitric acid at about 10°; the mixture was allowed to stand about two hours, and its temperature was then raised to from 20° to 30°, and kept between these limits during the addition of another equal weight of nitric acid; as this second part of the nitration did not seem to proceed so rapidly as the first, the mixture was allowed to stand twelve hours, then poured into a large volume of water: the nitro-compound separated as a white precipitate, which was filtered and washed till free from sulphuric acid. The dried product proved to contain about 75 per cent of a substance soluble in cold acetic acid to the extent of only about 1 per cent, which, by repeated re-crystallisations from acetic acid or a mixture of phenol and alcohol, was obtained of a constant melting point (244–245°). A nitrogen determination gave 10.89 per cent; that calculated for tetranitrophenolphthalein, $C_{20}H_{10}O_{12}N_4$, is 11.2.

Tetranitrophenolphthalein is difficultly soluble in most ordinary solvents; it forms pale yellow indistinct crystals, readily soluble in alkalis; salts of the heavy metals, as barium, lead, and silver, precipitate its neutral solution. The sodium salt is a yellow dye-stuff, sold under the name of aurotine.

On alkaline reduction it yields an unstable blue colour. It was also observed that when phenolphthaleinsulphonic acid (*Annalen*, ccii., 73) was treated with 2 mol. proportions of nitric acid in presence of sulphuric acid, it yielded a soluble nitrosulphonic acid, but when 4 mol. proportions of nitric acid were used and the temperature was allowed to rise to 30° C., the product was for the most part insoluble in water and consisted simply of impure tetranitrophenolphthalein.

The author thanks Mr. F. Moore, B.Sc., for the analytical figures which are quoted, and Dr. Dreyfus, Managing Director of the Clayton Aniline Company, where the experiments were made, for permission to publish the results.

105. "*A Method for the Preparation of Acetylene.*" By MORRIS W. TRAVERS.

Maquenne has recently published (*Compt. Rend.*, 1892) an account of a method of preparing acetylene by the interaction of water and barium carbide, the carbide being made by reducing barium carbonate with magnesium in the presence of carbon, a method which affords about half the calculated quantity of barium carbide. Wöhler obtained calcium carbide by heating calcium-zinc alloy with carbon in a graphite crucible.

Calcium carbide may be prepared in quantity by reducing calcium chloride with sodium in the presence of carbon. The operation is conducted as follows:—45 grms. of sodium are placed at the bottom of a deep iron bottle, and an intimate mixture of powdered gas carbon and calcium chloride which has been well dried on a hot iron dish is then introduced; the top of the bottle, furnished with a long neck, having been screwed on, the bottle is heated to bright redness during half an hour; it is then removed from the fire, stoppered, and cooled with water. When broken away from the bottle, the product is dark grey in colour and consists of sodium chloride, calcium carbide, and the excess of carbon added to render the mass less compact; usually about 16 per cent of carbide is formed, which is half the theoretical quantity. In practice, 1 grm. of sodium thus converted into carbide is found to yield 240 c.c. of acetylene instead of 487 c.c. the calculated equivalent quantity.

PHYSICAL SOCIETY.

Annual General Meeting, February 10th, 1893.

WALTER BAILY, M.A., Vice-President, in the Chair.

THE reports of the Council and Treasurer were read and approved, copies of the balance sheet being distributed to members. From the former it appears that the Society now numbers 371 ordinary members and twelve honorary members, and during the past year the Society has lost six members by death, viz., the Rev. T. Pelham Dale, Dr. J. T. Hurst, B. Loewy, C. E. Walduck, G. M. Whipple, and P. W. Willans. Obituary notices accompany the report.

The Treasurer's statement shows the financial condition of the Society to be satisfactory.

A cordial vote of thanks to the Committee of Council on Education for the use of the rooms and apparatus of the Royal College of Science was proposed by Mr. SHELFORD BIDWELL, seconded by Mr. BLAKESLEY, and carried unanimously. A similar vote was accorded to the auditors, Mr. H. M. Elder and Mr. A. P. Trotter, on the motion of Dr. GLADSTONE, seconded by Prof. S. P. THOMPSON. Prof. RAMSAY proposed a vote of thanks to the Officers of the Society for their services during the past year; this was seconded by Prof. FULLER and carried. Prof. PERRY responded.

The following gentlemen were declared duly elected to form the new Council:—

President—Prof. A. W. Rücker, M.A., F.R.S.

Vice-Presidents—Walter Baily, M.A., Major-General E. R. Festing, R.E., F.R.S., Prof. J. Perry, D.Sc., F.R.S., Prof. S. P. Thompson, D.Sc., F.R.S.

Secretaries—H. M. Elder, M.A., 50, City Road, E.C., and T. H. Blakesley, M.A., M.Inst.C.E., 3, Eliot Hill, Lewisham, S.E.

Treasurer—Dr. E. Atkinson, Portesbery Hill, Camberley, Surrey.

Demonstrator—C. Vernon Boys, F.R.S., Physical Laboratory, South Kensington.

Other Members of Council—Shelford Bidwell, M.A., LL.B., F.R.S., W. E. Sumpner, D.Sc., Prof. G. Fuller, J. Swinburne, Prof. J. V. Jones, M.A., Rev. F. J. Smith, M.A., Prof. G. M. Minchin, M.A., L. Fletcher, M.A., F.R.S., Prof. O. Henrici, Ph.D., F.R.S., James Wimshurst.

In response to invitations for suggestions regarding the working of the Society, Prof. S. P. THOMPSON said all must appreciate the efforts of the late Council, and particularly of the honorary secretaries, in making the Society better known. But he could not help thinking that there were many persons among teachers of physics and scientific amateurs whose active sympathies it was desirable to engage, who were not yet associated with the Society. Perhaps the time of meeting was not convenient for all, but he thought much might be done by freely circulating particulars of what was going on at the meetings. The daily papers merely announced the meetings, but said nothing as to the place of meeting or the papers to be read. In his opinion the Society did not take the position in the scientific world to which it was entitled, and he wished to inspire members with a determination to bring its claims prominently forward.

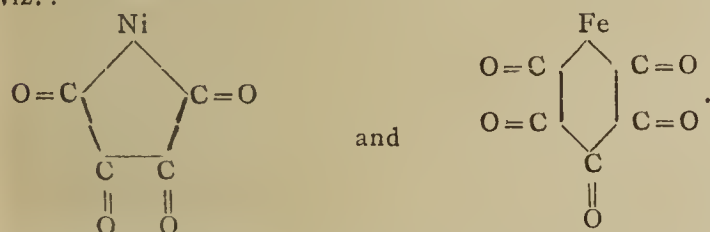
Mr. BLAKESLEY pointed out that almost all the scientific and technical papers gave full announcements of the meetings and of the papers to be read.

Mr. W. F. STANLEY said Friday afternoon was not convenient for scientific men engaged in trade.

The meeting was then resolved into an Ordinary Science Meeting, and Mr. C. E. GROVE was elected a member of the Society.

Dr. J. H. GLADSTONE, F.R.S., read a paper on "*Some Recent Determinations of Molecular Refraction and Dispersion.*"

The paper relates to the new metallic carbonyls, the metals indium and gallium, sulphur, and to liquefied oxygen, nitrous oxide, and ethylene. The carbonyls were found to be extremely refractive and enormously dispersive. For iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, the molecular refraction for the line α of hydrogen was found to be about 68.5, and the molecular dispersion between γ and α of hydrogen 6.6. For nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$, the corresponding numbers are 57.7 and 5.93. In discussing the results it was pointed out that if the molecular refraction of CO be taken as 8.4, the value expected in organic substances, then the atomic dispersion of nickel and iron come out greatly in excess of the known values as determined from solutions of their salts. The author considers the most probable explanation of the excessive refractions and dispersions of the carbonyls is to be sought in the peculiar arrangement of the CO, and on optical as well as chemical grounds accepts the ring formulæ indicated by Mr. Mond in his lecture at the Royal Institution, viz.:—



On this supposition the molecular refraction of CO comes out 11.9 from the nickel compound and 11.3 from the iron ore, whilst the molecular dispersion ($\gamma - \alpha$) is about 1.3 in each case. For indium and gallium the atomic refractions, calculated from latest data, are 13.7 and 11.6 respectively. Sulphur has been examined in the states of solid, liquid, and gas, and also in simple chemical combination, and in solution, all the resulting numbers for its atomic refraction being remarkably concordant. For the line C this is about 16. The dispersions in all the different states are also in close agreement. Numbers relating to carbon and chlorine are also given.

The specific refractions of oxygen, nitrous oxygen, and ethylene in the liquid states had been recently determined by Profs. Liveing and Dewar. For liquid oxygen the refraction equivalent (3.182) differs little from that deduced from gaseous oxygen at ordinary temperatures (3.0316), and also corresponds fairly closely to the 3.0 obtained by Landolt from organic compounds. Liquid nitrous oxide gave 11.418 and 11.840 as the molecular refractions for the red ray of lithium and the line G respectively. In discussing these numbers it was pointed out that nitrogen in nitrous oxide was not in the same condition as nitrogen in ammonia. The latest determinations with liquid ethylene gave the molecular refraction for the line A as 17.41, the theoretical value being 17.40, thus showing very close agreement.

Mr. E. C. C. BALY made a communication on "*Separation and Striation of Rarefied Gases under the Influence of the Electric Discharge.*"

On examining with a spectroscopic vacuum tube, containing a small quantity of hydrogen, the author noticed that the hydrogen lines were strongly visible in the negative glow, but could not be seen in the body of the tube. This observation was confirmed by examining other tubes, and seemed to point to a separation of gases in the tube. From subsequent experiments it also appeared that the striæ were due to this separation. By using a double tube containing a mixture of carbon dioxide and hydrogen, whose parts were connected by a narrow neck which could be sealed, and the parts detached, the gases were fractionated by the discharge. After sealing off, the spectra of the two parts were examined; the one that had formed the positive pole showed only a trace of hydrogen, whilst the other showed it brilliantly. Other mixtures gave similar results, and the separation was found not to depend on the relative molecular weights of the gases. A

very close connection between separation and striæ was noticed, the two phenomena always occurring together. On using a tube with a very minute negative electrode to avoid the negative glow, neither striation nor separation took place, but on reversing the current so as to make the large electrode the negative one, both phenomena became well marked. If the author's views were correct a pure vapour or gas should not striate. Pure mercury vapour gave no striæ, but on allowing a small quantity of other gas to pass into the tube they at once appeared. Pure vapours of iodine, sulphur, arsenic, and mercuric iodide gave similar results. Attempts to prepare a tube containing pure hydrogen which should not striate were not perfectly successful, but the striations usually seen in hydrogen tubes were reduced so as to be barely distinguishable. The author therefore concludes: 1. When an electric current is passed through a rarefied mixture of two gases, one is separated from the other and appears in the negative glow. 2. That striæ are caused by the separation of the two gases, and do not occur in a single pure gas or vapour.

Mr. BLAKESLEY read a communication from Dr. W. Crookes relating to Mr. Baly's paper, and pointing out that in his Presidential Address to the Institution of Electrical Engineers in January, 1891, he had given reason for believing stratification due to the gas not being homogeneous. He had also shown that the character of the stratification depended on the potential of the discharges.

Prof. RAMSAY said no proof had been given that electrolysis occurred in such tubes, and it was an open question whether molecules would convey electricity as ions do. So far as was seen, no ions existed in vacuum tubes. Possibly the stratifications resulted from collisions of molecules giving higher temperatures at some parts of the tube; but this was doubtful.

Mr. ENRIGHT thought the analogy with electrolysis was not quite clear, for in a mixture of simple gases the elements were not combined chemically, and electrolysis involved the splitting up of chemical compounds.

Prof. S. P. THOMPSON hoped the author would continue his important work and clear up the doubtful points in vacuum tube phenomena. Some difficulty existed in classifying the separation of the gases with electrolysis; for in the latter, the effects were only visible at the electrodes and not in intermediate portions of the substance. The question whether vacuum tube discharges were strictly analogous might be tried by fractionating through more complicated tubes. Prof. Schuster has considered the analogies in his Bakerian Lecture, and published some important results, some of which tended to show that wandering ions existed in vacuum tubes through which discharges were being passed.

Referring to Prof. Ramsay's remarks about molecules not carrying electricity, he (Prof. Thompson) said that electric winds were phenomena which pointed to the opposite conclusion. Similar convective action also occurred in turpentine and other insulating liquids. He wished to know whether the author had tried if a low voltage (say 100 volts) applied for a long time to a vacuum tube, would produce separation of the contained gases. Poiret's phenomenon of electric osmose seemed to have some bearing on the subject, as also Faraday's observations on the movements of scraps of silk in turpentine, and showing that in non-conducting liquids there were phenomena somewhat analogous to electrolysis.

Prof. RAMSAY said that if indigo be put in a poor conductor, such as distilled water, and the mixture subjected to electrolysis, all the blue colour became concentrated about one electrode, whilst if arsenic sulphide be similarly treated, the colour went to the other pole. On mixing the two solutions, all coagulates and goes down. He could give no explanation of these remarkable effects.

Mr. BLAKESLEY inquired whether tubes which had been kept some time showed the same phenomena as immediately after sealing.

In his reply Mr. BALY said the striæ in some tubes had very peculiar shapes, some showing discs and others showing cones alternately base to base and apex to apex. He had tried the experiment with complicated tubes as suggested by Prof. Thompson, but the result was not conclusive.

CORRESPONDENCE.

THE ETHICS OF "ABSTRACTION."

To the Editor of the Chemical News.

SIR,—There is an abstract of a paper read by Mr. E. Lodge before the Society of Dyers and Colorists in the number of the *Jour. Soc. Chem. Ind.* for July, 1892, and this abstract concludes with the remark: "Several of the author's statements are at variance with the results of other experimenters and require confirmation." I should like to draw attention to two points raised by a study of this sentence—its construction and its origin.

In the first place, it seems to me that we have not to consider the author's "statements," but the results of the author's experiments with regard to the results of other experimenters. In the second place, the other experimenters should be named in order that the student or technologist may have an opportunity of examining the question for himself. In the third place, it does not appear to be absolutely correct to assume that Mr. Lodge's results require confirmation, it would be more fair to say that a revision of the work on the subject in question is necessary.

The abstract conveys no clue as to the origin of the remark with which it concludes. It may have its origin from one of three sources. Mr. Lodge may have remarked that his results differed from those obtained by others; a discussion following the paper may have brought something to light with regard to the results of other experimenters; or the abstractor himself may have added the remark on his own responsibility. In any of these cases the abstract should carry with it an indication whereby the value of the practically adverse criticism may be determined.—I am, &c.,

"DYER."

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—The proposal to erase the letters F.C.S. from the Register of the Institute of Chemistry will surely be regarded by most persons as a slight upon the older parent Society, and this in spite of all disclaimers of any such intention.

May we not hope that on reflection the Institute will resume its filial relation to the Chemical Society by rescinding the resolution?—I am, &c.,

G. A. KEYWORTH.

Hastings, Feb. 20, 1893.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 6, February 6, 1893.

Preparation of Carbon under a Strong Pressure.—Henri Moissan.—The author refers the varieties of carbon

to three chief types: diamond, graphite, and amorphous carbon, and he lays before the Academy an account of the preparation of carbons of a high specific gravity. As a preliminary he has studied the composition of the ash, of the diamond, of bort, and of carbonado. He shows the existence of graphite, of carbonado, and of microscopic diamonds in the "blue earth" of South Africa, and the existence of the diamond in the meteorite of Cañon Diablo. He has studied the solubility of carbon in magnesium, aluminium, manganese, chrome, uranium, silver, platinum, and silicon. Operating on a mixture of diamond, graphite, and amorphous carbon he has removed all matter except diamond by successive treatment with hydrochloric or nitric acid, boiling sulphuric acid, hydrofluoric acid, and a mixture of potassium chlorate with nitric acid. He succeeds by these means in separating from the "blue earth" a variety of carbon hard enough to scratch ruby, and of the specific gravity of diamond. It burns in oxygen, yielding 3—3.5 carbonic acid.

Reproduction of the Diamond.—C. Friedel.—A discussion on the foregoing paper.

Study of the Chromium Fluorides.—C. Poulenc.—The author has obtained anhydrous and crystalline chromium mono- and sesquifluorides. He also describes a new hydrated chromium fluoride, $\text{Cr}_2\text{F}_{6.7}\text{H}_2\text{O}$, and a new method of preparing the double potassium-chromium fluoride, $\text{Cr}_2\text{F}_6.6\text{KF}$.

New Process of Soldering for Aluminium and various Other Metals.—J. Novel.—Aluminium is soldered with the alloy given below, with the ordinary tinman's soldering iron, or with the blowpipe. It does not oxidise or discolour the metal. The following solders are employed for aluminium:—No. 1. Pure tin; melts at 250° . No. 2. Pure tin 1000 parts; fine lead 50 parts. Melts at from 280° to 300° . No. 3. Pure tin 1000 parts; pure zinc 50 parts. Melts at from 280° to 300° . These three solders may be used in the manufacture of aluminium trinkets. For the following two solders the soldering iron should be made of pure nickel. No. 4. Pure tin 1000 parts; pure copper 10 to 15 parts. Melts at from 350° to 450° . No. 5. Pure tin 1000 parts; pure nickel 15 parts. Melts at from 350° to 450° . No. 6. Pure tin 900 parts; pure copper 100 parts; bismuth 2 to 3 parts. Melts at from 350° to 450° , and is recommended for soldering aluminium bronze.

Action of Acetic Acid and Formic Acid upon Turpentine.—MM. Bouchardat and Oliviero.—For this paper we refer to the original.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 83.

Experiments in the Filtration of Sewage performed by the Sanitary Council of the State of Massachusetts.—(Taken from the *Journal of the Franklin Institute*).—The only novelty in these experiments, which are described as very successful, consists in the sewage being run in so gradually that the beds were never entirely submerged. No analyses are quoted.

Zeitschrift für Analytische Chemie.
Vol. xxxii., Part 1.

Source of Error in the Ultimate Analysis of Organic Compounds, especially Nitrogenous.—G. Neumann.—As various authors allege—among others A. Leduc—ignited copper can absorb hydrogen. The author has observed this behaviour, but he has not been able to verify the statement of Thudichum and Hake and of Vortmann that carbon dioxide, if passed over ignited copper which has been reduced with hydrogen, is capable of expelling all the hydrogen. On the contrary, he proves that besides the retention of a part of the hydrogen on

subjecting the copper to a current of carbon dioxide, there occurs an absorption of carbon dioxide.

Modification of the Dumas's Method for the Determination of Nitrogen.—F. Blau (*Monatshefte für Chemie*).—This paper requires the two accompanying figures.

Specific Gravity of Acetone, Its Solvent Power for Certain Inorganic Salts, and Its Solubility in Aqueous Solutions of Sugar.—W. H. Krug and Mc Elroy.—(From the *Four. Anal. Chem.*).

Separation of Salicylic and Benzoic Acids.—J. Schaap (*Ned Tyds. Pharm.*).—Already inserted.

Reverdin and De la Harpe's Method for Determining Aniline and Monomethylaniline.—M. Giraud.—A mixture of acetic anhydride and dimethylaniline kept in well closed vessels remains for a week without decomposition.

Determination of the Acidity of Wine derived from Fixed and Volatile Acids.—J. A. Müller.—This paper will be inserted in full.

The Detection of Cherry Juice in Raspberry.—Wimmer (*Pharm. Zeit.*).—The author adds basic lead acetate and filters. If a few per cents of cherry juice are present, the filtrate is blue with a reddish reflection. Pure raspberry juice, if similarly treated, yields a filtrate which is nearly colourless. The author finds that this test must be applied with much caution and in presence of pure comparative samples.

Pure Culture of Motile Bacteria.—R. Kluge and G. Marpmann.

Diagnosis of the Typhus Bacillus.—J. Weyland.

Staining the Bacilli of Tubercle.—Neumann-Wender.—These three papers will be inserted in full.

Sophistication of Butter.—H. W. Wiley.—(From the *Four. Anal. Chemie*).

Analysis of Cheese.—Arnoldo Maggiora (*Archiv. für Hygiene*).—The author determines moisture, fat, by extracting the dry residue with petroleum ether in Soxhlet's apparatus, crude proteine, determining nitrogen by the Kjeldahl process and multiplying by 6.25; pure proteine, separating the albumenoid substances by Stutzer's process, and determining its nitrogen by the Kjeldahl process, multiplying finally by 6.25; ammoniacal nitrogen, amido-nitrogen, and ash.

Advances in the Fat, Oil, Soap, and Naphtha Industries.—D. Holde (*Chem. Zeit.*).—A pure compilation.

Examination of Wool-Fat (Lanoline).—H. Helbing and F. W. Passmore.—The authors saponify by covering 5.3 grm. anhydrous wool-fat with 20 c.c. alcoholic potass-lye in a strong flask containing about 50 c.c., stoppering and heating for two hours to 100° with occasional agitation.

Detection of Resin-Size in Paper.—W. Harrberg (*Chem. Zeit.*).—A piece of the paper is laid over a hollow support (a tumbler), and about four to six drops of ether are let fall upon the middle of the leaf. If resin is present a resinous border will appear after the ether has evaporated.

Valuation of Indigo.—A. Müller (*Chem. Zeitung*).—The author stirs up 0.5 grm. of the sample in the finest powder with 10 grms. sulphuric monohydrate (obtained by mixing seven parts of sulphuric acid at 95.5 per cent with three parts of fuming sulphuric acid containing 30 per cent of sulphuric anhydride), converts it into the disulpho-salt by means of heat, dilutes it when the reaction is completed to 1 litre, and titrates with permanganate in the usual manner until the olive tone of the liquid has disappeared.

Determination of the Fineness of Powdered Sulphur.—Chancel (*Weinlaute*).—For this paper we must refer to the original.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Medical, 8.30.

TUESDAY, 28th.—Institute of Civil Engineers, 8.

— Photographic, 8.

— Royal Medical and Chirurgical, 8.30.

— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psychophysiology," by Prof. Victor Horsley, F.R.S.

— Society of Arts, 8. "Russia as a Field for Tourists," by Sir Edward Braddon, K.C.M.G.

WEDNESDAY, March 1st.—Society of Arts, 8. "Tele-Photography," by Thomas R. Dallmeyer.

THURSDAY, 2nd.—Royal, 4.30.

— Royal Society Club, 6.30.

— Royal Institution, 3. "The Factors of Organic Evolution," by Prof. Patrick Geddes.

— Chemical, 8. "Notes on Optical Properties as Indicative of Structure" (postponed), by H. E. Armstrong. "The Ethereal Salts of Active and Inactive Glyceric Acid," by P. Frankland and J. MacGregor. "Limits of Accuracy of Gold-bullion Assay, and the Losses of Gold Incidental to it—The Voatilisatation of Gold," by T. R. Rose. "The Interaction of Alkali-cellulose and Carbon Disulphide—Cellulose Thiocarbonates," by C. F. Cross, E. J. Bevan, and C. Beadle. "A New Atomic Diagram and Periodic Table of the Elements."

FRIDAY, 3rd.—Royal Institution, 9. "Sculpture, considered apart from Archæology," by George Simonds.

— Geologists' Association, 8.

— Quckett Club, 8.

SATURDAY, 4th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

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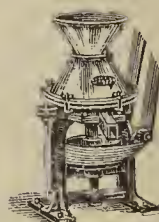
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THE CHEMICAL NEWS.

VOL. LXVII., No. 1736.

A SOURCE OF ERROR IN THE ULTIMATE ANALYSIS OF ORGANIC SUBSTANCES.

By G. STILLINGFLEET JOHNSON.

It is gratifying to me to find that some work which I did seventeen years ago is receiving confirmation in Germany. In the *Zeit. Anal. Chemie* (vol. xxxii., Part 1) G. Neumann comes to the conclusion that hydrogen gas, occluded in copper turnings, is a source of error on the side of excess in hydrogen determinations.

In the *Chem. Soc. Jour.* (1876, i., 178), I first published a notice of this source of error, and in the same journal (May, 1879) I followed it up with a second paper "On the Occlusion of Hydrogen by Copper." In this second paper the following facts were proved.

1. Metallic copper occludes very varying quantities of hydrogen, according to the state of its surface.
2. Alternate oxidation and reduction of the same copper tends gradually to diminish the weight of occluded hydrogen.
3. Copper, which has occluded hydrogen, parts with its occluded gas when heated to redness in pure nitrogen.
4. Copper, which has occluded hydrogen, does not part with its occluded gas when heated to redness *in vacuo*.
5. Perfectly pure copper occludes no hydrogen whatever. The presence of sulphur appears to increase occlusion.
6. A good test for occluded hydrogen in copper is to boil the metal with solution of potassium chlorate, which is reduced to chloride.

It may be interesting to indicate the general method of procedure which I at present adopt to avoid this error.

- (1) The copper employed is selected as *free from sulphur* as possible.
- (2) The copper is oxidised and reduced alternately several times before using.
- (3) The substance is burnt in a boat, behind which is a second boat containing reduced copper, and a third boat containing fused KClO_3 . In front of the boat with the substance is granulated copper oxide, and in front of that the reduced copper for reduction of the oxides of nitrogen.

The whole tube is now heated to redness, except the portions occupied by the boats containing the KClO_3 and the substance to be burned, and a slow stream of dried air is passed through until all the reduced copper behind the substance has been oxidised. The weighed apparatus is then adjusted in front and the combustion proceeded with. My hydrogen determinations are (with the above precautions) usually within 0.1 per cent of the theory.

King's College, London, Feb. 20, 1893.

THE SOLUTION OF AIR IN SEA-WATER.

By A. E. RICHARDSON, B.A., F.C.S., A.M.I.E.E.

It is a well-known fact that the amount of gas capable of being held in solution by a given liquid is directly proportional to the pressure exerted, unless chemical combination takes place between the gas and the solvent. But the pressure at any point within a fluid, which is incapable of being compressed, is proportional to the depth of that point below the surface of the fluid. Consequently, it is obvious that the water deep down in the ocean must be capable of dissolving greater quantities of air than water at the surface.

To illustrate this point, let us take an extreme case and roughly calculate the volume of air which could be absorbed by unit volume of water deep down in the sea. The depth of the Pacific Ocean is known to be as much as 40,000 feet (or $7\frac{1}{2}$ miles) in at least one place.

First, we will calculate the pressure exerted upon a cubic foot of water at that depth. Assuming that the specific gravity of sea-water is roughly 1.026, a cubic foot of sea-water will weigh 1026 ozs. (a cubic foot of distilled water is generally taken as weighing 1000 ozs.). Then the pressure exerted per square foot at a depth of 40,000 feet will be—

$$40,000 \times 1026 \text{ ozs.} = 40,000 \times \frac{1.026}{16} \text{ lbs.}$$

Hence the pressure per square inch will amount to—

$$\frac{40,000}{144} \times \frac{1026}{16} = 17,812\frac{1}{2} \text{ lbs.}$$

The pressure due to one atmosphere may be roughly taken as 15 lbs. per square inch. Thus the pressure at a depth of 40,000 feet is equivalent to that of 1187 atmospheres. This, with the pressure due to the air above, amounts to 1188 atmospheres.

It must be borne in mind that this is only an approximate calculation. For instance, the density of sea-water is taken at a rather low figure, and no allowance is made for the compressibility of sea-water under great pressures.

Accepting, however, 1188 atmospheres as the approximate pressure at the stated depth, let us calculate the volume of air which a unit volume of the water would be capable of dissolving under this pressure.

I have no data at hand for the absorption coefficients of sea-water for oxygen and nitrogen or for air, so I will take the coefficients for pure water. Here again an error will arise, for sea-water cannot absorb so much air as ordinary water; for it has been found that in solutions of different substances the solubility of gases is in most cases diminished.

One volume of water at normal temperature and pressure absorbs about 0.0245 volume of air. With the temperature remaining constant the volume of gas absorbed remains the same under all pressures. But this volume of air, under a pressure of 1188 atmospheres, would occupy a volume of 0.0245×1188 under normal pressure. This quantity amounts to 29.106 volumes. Hence, a cubic foot of water at a depth of 40,000 feet is capable of absorbing 29 cubic feet of air measured at normal pressure.

Since a c.c. of air weighs 0.00129 grms. 29 c.c. will weigh 0.037 grm. That is to say, the water in question would be capable of dissolving about 1.27th of its own weight of air. Nor does there seem any reason to suppose that this amount of air is not absorbed, for the atmospheric gases must permeate the whole of the ocean's depth in order that deep sea fishes may obtain the oxygen necessary for the preservation of their existence. At a depth of 1380 feet water absorbs its own volume of air (measured at atmospheric pressure). Thus in all water below this depth there is dissolved more than its own volume of air. We have then a second but submerged atmosphere.

In this most marvellous submarine atmosphere are vast quantities of air stored away,—how vast it is difficult to estimate. Remembering that three-fourths of the face of the earth is covered by water, one is apt to conclude that there is almost as much air hidden away in the ocean's depth as is found above its surface. What effect such great pressures have upon the solvent powers of the water for solid constituents it is doubtful to say. Probably the solvent powers are much modified by the presence of such quantities of dissolved gases. It is possible that such considerations as the foregoing have already appeared in print. As, however, I have never read or heard of such suggestions, I venture to bring the question before your readers.

Dorking, Surrey.

BEHAVIOUR OF THE GADOLINITE EARTHS WITH POTASSIUM CHROMATE.

By G. KRÜSS and A. LOOSE.

(Continued from p. 89).

Preparation of Didymium Oxide by Means of Potassium Chromate from a Mixture of the Gadolinite Earths.

It was investigated whether and how quickly didymium oxide could be obtained by repeated precipitation in the cold with potassium chromate. The institution of these experiments seemed interesting with reference to the renewed examination to which didymium has been submitted since its scission into neodymium and praseodymium.

For a preliminary experiment five different earthy mixtures were united, containing all the erbia and didymia earths (except yttria), and on determination of the equivalents showing the following values for R. 111'7, 113, 115'6, 120'9, and 135'5, in the mean = 119'3. They were converted into a nitrate solution. After neutralising the excess of acid the liquid was precipitated with potassium chromate in the cold, and the earth con-

tained in the precipitate was examined. It was a R = 133'7. It was converted into a nitric solution, with which the chromate precipitation was repeated. On determining the combining-weight, the material obtained was R = 137'7, and after again repeating the chromate treatment R = 142. After these three operations the didymium spectrum had become considerably more intense.

This was an inducement to submit to the above method for preparing didymium oxide, a material which, beside small quantities of samarium and holmium, contained erbia, didymia, and yttria in approximately equal proportions. The nitrate solution of this material displayed the spectrum:—

λ .	Strength of absorption.	Symbol.
728'3.. ..	Very strong	Di α
679'4.. ..	Faint	Di β
579'2.. ..	Very strong	Di γ
523'1.. ..	Strong	Er β
512'2.. ..	Fading	Di ϵ
482	Distinct	Di ζ
477'7.. ..	"	Sm β
469	"	Di η
463'2.. ..	"	Sm β
445'1.. ..	Strong	Di δ
428'5.. ..	Very distinct	X η

Hence it contained much erbium and didymium, and on determining its equivalent it was found to be R = 131'5. Much yttria is therefore present doubtless in a proportion approximately equal to the erbia and didymia, since—

$$\frac{(\text{Er} = 166) + (\text{Di} = 146) + (\text{Y} = 90)}{3} = 134 \text{ R,}$$

—a mean value which does not greatly differ from the value R = 131'5 as ascertained. This material was resolved into four fractions by precipitation in the cold with K₂CrO₄.

The first and the second fraction both gave on analysis a R = 146, where the oxide before conversion into sulphate had been heated in a current of hydrogen until its weight was constant. The third fraction gave R = 138'3, and the fourth R = 126'2.

The first and second fraction had therefore given at once the former atomic weight for didymium, perhaps slightly too high. In the spectrum the Er β line was no longer visible, though the Er β line was still present. These two fractions were combined and the chromate method was again applied, when the Er β line appeared fainter and the didymium oxide showed on analysis R = 145'3.

We may consider the atomic weights hitherto found for didymium:—Marignac in 1853 made it 144; Hermann in 1860 142'44; Erk found it about 143, and Zschiesche 141'2, both in 1870; Cleve in 1874 found it 147'01, and Marignac in the same year from 143'6 to 144. Brauner in 1882 gave the value 146'58, which he afterwards rejected and adopted 145'52. Subsequently he split up the apparently purest didymium into earths, the atomic weights of which varied from 143'3 to 149'4. According to him the increases of the atomic weights were due to the presence of impurities of erbium, holmium, and samarium. Lastly, Auer von Welsbach on decomposing didymium found for praseodymium 143'6 and neodymium 140'8.

According to these results the atomic weight of didymium as found by the chromate method seems rather too high. The cause may easily be found in traces of samarium and erbium which adhere obstinately, but from which in case of need it may be purified by fractionated precipitation with ammonia. Otherwise the oxide obtained agreed well with the descriptions given for ordinary didymium oxide. It was of a dark brown colour as it was obtained by Mosander, Hermann, and Zschiesche. On reduction in a current of hydrogen the colour changed to a dirty pale grey. The excess of oxygen in the brown earth amounted in two determinations of pure specimens to 0'447 and 0'5 per cent. Hermann and also Marignac obtained an excess of 0'446, 0'32, and 0'88. Frerichs and Smith (*Liebig's Ann.*, 191) concluded that this excess was 7'13 per cent, but they were long ago refuted by Cleve, Nilson, and others. The sulphate of the oxide obtained by means of chromate generally appeared as a sintered cake of felted needles of a violet colour, resembling that of *Colchicum autumnale*. A borax bead was reddened by the oxide.*

We may also obtain very pure didymium oxide (in the ordinary sense of the word) from an earthy nitrate solution not too poor in didymium by a single precipitation with potassium chromate in the cold. If the earthy material contains but a scanty proportion of didymium, the earth can be isolated only by a treatment with chromate several times repeated.

Finally, to explain the reaction of potassium chromate and didymium nitrate, the following experiment was tried: As the didymium precipitate thrown down by K₂CrO₄, corresponding to the potassium didymium sulphate precipitate, might possibly consist of a potassium didymium chromate, about 0'3 gm. of neutral didymium sulphate was precipitated with a very concentrated solution of potassium chromate of a known strength, whereby the didymium was completely separated out. After making up the solution to 250 c.c., and allowing the precipitate to subside, 10 c.c. of the supernatant potassium chromate solution were taken out by means of a pipette. A determination of the potassium present showed that all the potassium used as chromate was present in the solution. Hence no formation of a double salt takes place.—*Zeit. für Anorganische Chemie*, vol. iii., p. 92.

Society of Arts.—Prof. Chandler Roberts-Austen will commence a course of three Cantor Lectures on "Alloys" at the Society of Arts on Monday next, March 6, at 5 o'clock. The remaining lectures will be given on the two following Monday afternoons at the same hour.

* "On the Interesting Property of Didymium Glass of Effecting an Absorption of Its Own Fluorescent Light." (See Lommel, *Ann. Phys.*, ii., 24).

DETERMINATION OF PHOSPHORUS IN IRONS AND STEELS.

By ADOLPHE CARNOT.

It is known that steels and irons of good quality can contain merely a very small proportion of phosphorus, and that a few ten-thousandths of that element suffice to modify greatly the properties of the metal. Hence the greatest importance is attached to an exact determination of the proportion of phosphorus.

Numerous methods have been proposed and give in different laboratories results which are often little accordant. The method which I am about to study, founded, like most others, on the use of ammonium molybdate, yields with less trouble more regular and more trustworthy results.

It differs from them (1) by the method of separation (and of determination) of the silicon, which is effected by means of sulphuric acid; (2) by the process for destroying the compounds of carbon in which chromic acid is employed; (3) by the nature of the final compound which is not magnesium pyrophosphate containing 27.928 per cent of phosphorus, but dried ammonium phosphomolybdate, which when obtained by a second precipitation under identical conditions presents a constant composition. It only contains 1.628 per cent of phosphorus, *i.e.*, seventeen times less than the pyrophosphate. Hence there is much greater accuracy in the determination.

We operate upon a portion of 5 grms. for irons, steels, and pure cast metal,—1 grm. or even 0.5 grm. being sufficient for phosphoriferous cast metals. The metal is treated with 40 c.c. of pure nitric acid in a large porcelain capsule, which is covered at once with an inverted funnel in order to avoid the projection of liquid drops. When the effervescence is at an end we heat gently to complete the action, and wash out the funnel with a little water, which is then received in the capsule. We add, whilst stirring up the liquid with a glass rod, 10 c.c. of concentrated sulphuric acid (2 c.c. per grm. of metal). There is produced a bulky pulp which re-dissolves on stirring and heating. We evaporate gently, either over a small rose-burner, stirring constantly for a quarter of an hour, or leaving it on the sand-bath for a longer time. The mass soon becomes pasty and then dry, becoming reduced to grains which are easily crushed with the stirring-rod.

It is placed on the stove and kept for two hours at a temperature of 120—125°, so as entirely to expel the nitric acid and render the silica throughout the mass quite insoluble. It is then re-dissolved in 50 c.c. of boiling water, and washed on a filter with an equal quantity of water, receiving the liquid in a litre flask.

The silica remains on the filter. It is generally coloured black or grey by graphite, and may be mixed with manganese peroxide. The latter is dissolved above another flask in a little concentrated hydrochloric acid and washed with hot water. We ignite to burn off the graphite and weigh the silica, which will have become white. This weight, multiplied by the coefficient 0.4667, gives an exact determination of the silicon, as in Drown and Shimer's method.

The filtrate contains the organic compounds derived from the transformation of the iron carbide under the action of the acids which might hinder the precipitation of the phosphoric acid. In order to burn the organic matter we add about 1 grm. of chromic acid and heat for half an hour to the temperature of ebullition. This operation has the advantage of certainly restoring to the state of orthophosphoric acid any trace of pyrophosphoric acid which may have been formed during the evaporation to dryness.

We then pour into the liquid 60—80 c.c. of a molybdic solution at 5 per cent prepared as usual, and keep it at 100° for two or three hours, the time necessary for a complete precipitation. It is allowed to settle and cool, and the liquid is decanted upon a filter and the deposit is

washed in the flask with luke-warm water containing 1-20th of its volume of molybdic solution until the washing water is only coloured a very slight rose by the addition of ammonium sulphocyanide, *i.e.*, until they contain merely negligible traces of iron.

We then dissolve the precipitate in the flask with 30 c.c. of ammonia, diluted with an equal volume of hot water, and placing the funnel with the filter upon a small flask holding 150 c.c., into which the acid liquid has been decanted, we introduce the ammoniacal solution. We wash the flask and the filter with 50 c.c. of boiling water, slightly ammoniacal, making use of the filter-pump.

The filter may retain small quantities of ferric hydrate and phosphate, which are re-dissolved in a few drops of hot, dilute nitric acid, which are subsequently added to the acid liquid.

The ammoniacal solution, filtered and cooled, is gradually neutralised by nitric acid, not raising the temperature above 40°. When a yellow precipitate begins to appear, which does not re-dissolve on stirring, we add as a surplus 3 c.c. of pure nitric acid and the small quantity of dilute acid which has served to wash the filter.

It is left for two hours at a temperature of about 40° for the precipitation of the ammonium molybdate. The liquid is then decanted upon a tared filter and replaced by water acidified with 1 per cent of nitric acid. After two or three washings the precipitate is placed upon the filter, washed with a little distilled water by means of the pump, dried at 100° in the stove, and weighed in a small special bottle with a wide mouth so that the filter may be introduced without breaking.

By this second precipitation of ammonium phosphomolybdate in conditions of temperature and acidity perfectly defined, we obtain a product of constant composition free from iron and from excess of molybdic acid, which is not regularly effected with the first precipitation. The weight of the phosphorus present is obtained by multiplying the weight of the dried precipitate by the coefficient 0.01628.—*Comptes Rendus*, vol. cxvi., p. 105.

ON CATHODIC RAYS IN GASES AT THE ATMOSPHERIC PRESSURE AND IN AN EXTREME VACUUM.*

By Dr. PHILIPP LENARD (of Bonn).

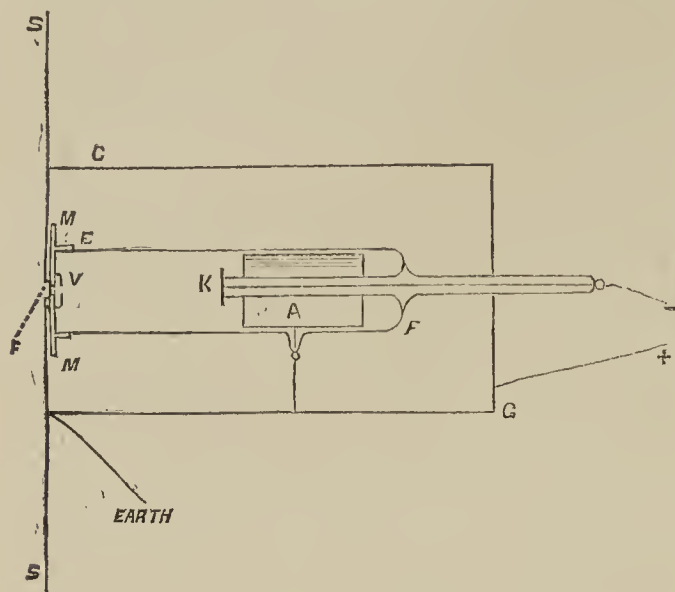
THE rays exciting phosphorescence, proceeding from the cathode of a Geissler tube, permeate thin metal leaves, as Herr Hertz has shown. If it were practicable to find a metallic leaflet of such a thickness that with perceptible permeability it still closes air-tight and is capable of bearing the pressure of the atmosphere on one side only, it would be sufficient to close an opening in the side of a discharge tube with such a plate in order to allow those rays a passage into the open air. This thought has been realised in the experiments which will in the sequel be briefly described to the Academy. It is shown that the cathode rays when once produced propagate themselves into space filled with air. Thus their observation is greatly facilitated, and it is possible to select and to vary the conditions of observation independently of those of their origin.

The Apparatus.

The figure shows a section of a convenient arrangement of the apparatus. E, E is the glass discharging tube, K the cathode, an aluminium disc of 12 m.m. in diameter, A the anode, which should preferably have a very large surface. Opposite to the cathode the tube is closed with a strong metal plate, M, M, which is perforated at F to the width of 1.7 m.m. Above this aperture there is cemented from without a hammered aluminium plate of 0.003 m.m. in

* A Paper read before the Royal Prussian Academy of Sciences at Berlin, in the Session of January 12, 1893.

thickness. We name this closing, which is permeable for cathode rays, but quite impermeable to air and light, the *window*, and the space to the left of it in the figure the space for observation. The distance of the cathode from the window is 12 centimetres; the latter is protected by the internal screen, *v*, from the extent of the discharge, and consequently from corrosion. Outwardly the large metal screen, *s, s*, is in conductive connection with the



window side, to which the sheet-metal case, *G, G*, is again connected. The case, the screen, and the anode, as also the positive pole of a large inductorium, are connected to the earth, whilst its negative pole is connected with the cathode. The arrangement selected keeps the space for observation almost perfectly free from light and from the electric powers of the discharge.

The most favourable exhaustion in the discharging tube is reached when the potential difference between its electrodes corresponds to a striking distance of three centimetres between balls in air. As regards the phenomena which appear in the observation space, I have been able to establish the following, in addition to some less important points.

Cathode Rays in the Open Air.

1. The cathode rays render the air faintly luminous. A halo of bluish light surrounds the window, and is moderately bright only on its surface. A strong odour of ozone is recognised.

2. Substances capable of phosphorescence, if held near the window, shine with their peculiar light on the side nearest the window. With an increasing distance from the window, the phenomenon rapidly decreases in intensity, and disappears at a distance of about six centimetres. Only the magnitude of the distance determines the brightness of the light; their direction is of no importance, which is not surprising, since cathode rays pass in a diffused manner through aluminium (H. Hertz, *Wied. Ann.*, vol. xlv., p. 31). Alkaline earthy phosphides, ordinary and uranium glass, calc-spar, fluor-spar, and other minerals, pentadecylparatolylketon, and asaron, all give out a light of the same colour and relative brightness as they do in exhausted spaces in the region of the cathode rays. The intensity is peculiarly strong with the alkaline earthy phosphides and the above-named carbon compounds. Among liquids, a drop of petroleum displayed its blue fluorescence. Metals, quartz, mica, and eosine gelatin (strongly excitable by light) remained non-luminous, as in exhausted tubes, as also aqueous solutions of eosine and fluoresceine, and the ethereal solution of chlorophyll.

All the phenomena of phosphorescence in the observation space cease if a magnet applied to the discharge

tube repels the cathode rays from the inner surface of the window.

3. A quartz plate, one-half m.m. thick and not too small, inserted at any place between the window and the phosphorescible body, causes the extinction of the light. An ordinary foil of gold, copper, or aluminium permits it to remain scarcely weakened. Whether a substance proves permeable or not depends entirely on the thickness of the stratum employed. I have met with no solid body which is perceptibly permeable at the thickness of one-fifth m.m. or upwards, but thin layers of almost all substances were partially permeable. Thus stout writing-paper, collodion films, aluminium foil even rolled to the thickness of 0.03 m.m., glass blown thin, and mica split very thin. In addition to the metal foils above mentioned, silk, paper, and soap bubbles form screens almost absolutely permeable; they show colours below the sixth order.

4. The atmosphere is a dull medium for cathode rays; they do not spread out in it rectilineally, but in a diffused manner. The phosphorescent action penetrates deeply into the shadow of an opaque body supposed to be projected from the window, and it is not possible to separate by means of diaphragms sharp rays of a centimetre in length. If there is a metal plate with a sharply defined aperture about 1 m.m. in width in the way of the cathode rays—say at a distance of 20 m.m. from the window—and if we examine the space behind the plate with a phosphorescible screen, we find a sharp bright figure of the aperture only close behind it; even at a distance of 3 m.m. the image is magnified five-fold and indistinct, and at a distance of 12 m.m. the screen is everywhere almost uniformly illuminated.

Cathode Rays in a Vacuum.

For the nature of the cathode rays it is a fundamental question whether their propagation depends on the presence of matter or if it takes place in void space. The impossibility of producing cathode rays in a complete vacuum has hitherto prevented the solution of this question. It is now possible to evade this hindrance; we produce the rays as heretofore, enclose the observation space with glass walls, and exhaust it.

The further the evacuation proceeds, the greater becomes the distances at which the phenomena of phosphorescence can be recognised, and the more distinctly the rays are simultaneously separated by a diaphragm. If that high degree of exhaustion is reached at which the cathode rays are generally studied, the phenomena of phosphorescence (which are now very bright) display on the glass side of the observation space a rectilinear extension in all directions from the window. The length of the rays, which are now almost sharp (30 c.m.), is only limited by the sides. From this exhaustion to the utmost possible there now occurs little more change. The rays seem to become still rather sharper, and the phosphorescence of the glass rather brighter. At this extreme exhaustion at which the mercurial air-pump ceases to act, even the most sensitive test for a gaseous residuum, the electric discharge, fails us. It is no longer possible to produce a discharge between the aluminium plates fused into the observation space. The interchange ensues externally along the glass side, although the distance of the electrodes is 20 c.m. To such imperceptible residues of matter we cannot ascribe any perceptible effects. If this is conceded, our experiment as to the nature of the cathode rays decides that they are processes in the ether. If they were processes in matter, that space would have been for them substantially impermeable. To the experiments in this section it must be remarked that at all degrees of exhaustion that admitted of a somewhat distinct formation of rays they are found to be strongly deflected by the magnet.

Cathode rays in Various Gases.

6. Various gases are turbid media in very different degrees; greater permeability is connected with greater

clearness. If we allow coal-gas to issue between the window and a phosphorescent screen, we perceive considerable clearing on the screen. If we now again fill the observation space, enclosed between glass sides, with hydrogen at ordinary pressure, the phenomena of phosphorescence extend for 20 c.m. from the window, *i.e.*, more than three times as far as in atmospheric air at the same pressure. At the same time we may, by means of a diaphragm, separate rays which up to about the length of 3 c.m. give moderately sharp phosphorescent spots. These rays, in hydrogen at a moderate pressure, are strongly deflected by the magnet. Oxygen is perceptibly less permeable than air and about equally turbid. Carbonic acid is much less permeable; in this gas all the phenomena are confined to distances below 4 c.m. from the window; rays, even of the length of a few millimetres, cannot be obtained.

To conclude from this behaviour of gases in the processes which make up the essence of the cathode rays extremely minute dimensions must come into consideration. Even to light of the shortest known wave-lengths matter seems to fill space continuously. But here the behaviour, even of elementary gases, is that of a non-homogeneous medium, each single molecule appears as a distinct obstacle. The number of mols. upon which the cathode rays impinge in equal volumes of different gases is always the same; whence we may say that hydrogen molecules obscure the ether much less than the molecules of oxygen, and these, in turn, less than molecules of carbon dioxide.

THE SIMULTANEOUS PRECIPITATION OF COPPER AND ANTIMONY BY THE GALVANIC CURRENT.

By W. HAMPE.

THE author shows that all the commercial brands of electrolytic copper which have been examined in his laboratory along with from 99.94 to 99.99 per cent of copper always contained small quantities of antimony, in good sorts from 0.007 to about 0.02. This fact shows that in the technical elaboration by means of electrolysis small quantities of antimony are always precipitated along with the copper.

Also in the determination of copper, as practised in the laboratories by the electrolysis of its sulphuric solution acidified with free nitric acid, antimony, if present, falls not only, as heretofore supposed, *after* the precipitation of the copper, but to a small extent also simultaneously. This fact must be taken into account in separations and in quantitative determinations of copper in order to avoid errors. The less antimony is present in the solution as compared with the copper, and the earlier the electrolysis is broken off the less antimony is precipitated along with the copper. The tension and the density of the current are not without influence. The following observations indicate the quantities of antimony deposited along with the copper under defined conditions.

1. A copper sulphate containing 25.09 per cent of copper, 0.0083 per cent of antimony (corresponding to a copper with 0.033 per cent of antimony), gave on the electrolysis of its saturated solution acidified with 20 c.c. nitric acid, with six Meidinger-Pincus globe elements, a copper containing 0.007 per cent antimony.

2. 45.896 grms. of an alloy of copper and antimony were treated with nitric acid, whereon the antimony partly passed into solution and partly remained undissolved as antimonious acid. Without separating the latter from the liquid it was evaporated down along with an excess of concentrated sulphuric acid until dense vapours escaped, and the residue was taken up with water and 20 c.c. nitric acid. After the undissolved part of antimonious acid was filtered off it was submitted to electrolysis, the current

being interrupted whilst the liquid was still distinctly coloured. It contained, as appeared on its further treatment with hydrogen sulphide, &c., still 0.3644 grm. copper along with antimony. The latter, along with the antimony of the undissolved residue, amounted to 0.2338 grm. The metallic deposit thus obtained electrolytically was of the finest rose colour, like chemically pure copper. Its weight was 45.284 grms. It was dissolved off the core by means of nitric acid, the solution was evaporated down with an excess of sulphuric acid until all nitric acid was expelled, the residue was taken up with water, and from the strongly acid solution the copper was thrown down by means of potassium sulphocyanide and sulphurous acid as a sulphocyanide.

The filtrate was worked up by well known methods, and was found to contain 0.009 grm. antimony which had been precipitated along with 45.275 grms. copper, so that the metallic precipitate had contained 0.0198 per cent antimony. From the above data the composition of the original alloy is computed as 99.441 per cent copper and 0.529 per cent of antimony. It also contained 0.015 per cent of iron.

It must be mentioned that the acids employed, prior to their use, had been freed from any antimony present. They had been diluted, treated with hydrogen sulphide, decanted, and again concentrated by evaporation.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING JANUARY 31ST, 1893.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, February 13th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 163 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

In respect to its general characters, and especially to the smallness of the proportion of organic matter present, the condition of the water supplied to the Metropolis during the month of January was, notwithstanding the unfavourableness of the season, entirely satisfactory. Thus, taking the Thames-derived water for comparison, the mean amount of oxygen required for oxidation was found to be 0.052 grain per gallon, as against a mean of 0.068 grain per gallon for the previous two months' supply. Again, the mean proportion of organic carbon was found to be 0.159 part in 100,000 parts of the water, with a maximum of 0.248 part in any single sample examined, as against a mean of 0.198 part and a maximum of 0.286 part in the previous two months' supply.

The condition of the water was, however, not uniform throughout the month. With the prolongation of the

frost—prevailing more or less continuously through the last week of December and first three weeks of January—and more particularly on the breaking up of the frost at the end of the third week of January, there was a noticeable, though indeed wholly unimportant, increase in the proportion of organic matter present both in the Thames-derived and in the Lea-derived water, as estimated alike by the “combustion” and “oxidation” processes. The increase, however, in the degree of colour tint of the water—usually, but not always proportionate roughly to the amount of organic matter present—was more decided, and in several of the samples of Thames water examined during the latter half of the month, reached and even exceeded the limit of the scale.

Despite the difficulties incident to the conduct of the process of filtration in time of frost, the whole of the 163 samples examined were found to be well filtered, clear, and bright.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.

ON STEEL CASTINGS.

By SERGIUS KERN, M.E., St. Petersburg.

IN Russia many works make at present very good steel castings. Principally open-hearth steel is used, though several works employ crucible steel. The Obouchoff Steel Works, near St. Petersburg, use crucible steel, preparing it in coke furnaces (four crucibles to each furnace). They have and always had extensive orders from the navy for gun-carriages. When we were connected with these works, the steel for casting the different parts of gun-carriages was prepared as follows:—Each crucible was loaded with forty pounds of puddled iron (0.12 per cent of carbon), and forty pounds of puddled steel of medium hardness (0.45 to 0.50 per cent of carbon). Finally, to this charge one-half to three-quarters of a pound of ferromanganese, containing 70 per cent of manganese, was added.

The crucibles are placed into the furnaces, and in about four and a half hours the charge is melted. Next to each crucible by means of an iron funnel is added two and a half pounds of silicon iron, containing 7 per cent of silicon. After a lapse of twenty minutes the casting of steel is commenced. The moulding sand is prepared from 85 per cent of white quartz sand, used for the formation of the open-hearth furnace lining at the same works, which is mixed with 15 per cent of good fire-clay and a small quantity of rye-flour, in order to render the moulds porous after heating them in the drying-stove.

The Poutiloff Iron and Steel Works, near St. Petersburg, use for small castings up to 10 pounds crucible steel, and for heavy castings open-hearth steel is used. They frequently receive orders from the navy for rudder-frames, stem-posts, stern-posts, shaft brackets, &c.

For instance, the Poutiloff Works lately executed the castings of a stem and stern posts for a gun-boat. Open hearth steel was used, and the addition before the casting consisted of ferrosilicon. The following are the chemical analyses:—

	Stem. Per cent.	Stern.
Carbon.. ..	0.13	0.15
Manganese.. ..	0.50	0.45
Silicon.. ..	0.27	0.25
Phosphorus.. ..	0.03	0.04
Sulphur.. ..	0.02	0.02

The mechanical tests gave the following results:—Stem-post, breaking strain 32.5 tons per square inch, elongation in eight inches 12.3 per cent; stern-post, breaking strain 34.8 tons per square inch, elongation in

eight inches 11.2 per cent. The Government commission found these tests satisfactory and adopted the castings. We prefer the use of ferrosilicon, or still better, silico-spiegel (10 per cent of silicon and 12 per cent of manganese). Sound and good steel castings are always obtained. After casting, the products must contain 0.25 to 0.30 per cent of silicon.

In general, when making steel castings we ought to remember that even in the last century Reaumur defined steel as a compound of iron and carbon, so that we must suffer the introduction of a small quantity of silicon only as an inevitable evil and then only as a necessity, in order to obtain a sound steel without forging the metal.

ON THE GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 92).

IN our calculation of the presumable effect of the sulphurous acid on the result of Dumas's syntheses, we neglected the error caused by the sulphurous acid contained in the surplus hydrogen which goes out of the water-receptacle through the action of the vitriol contained in the drying tubes included in the latter. As the quantitative effect of this sulphurous acid is difficult to predict, we tried to determine it by direct experiments. But, in doing so, we had our eyes more on our own “First Series of Syntheses” (*vide infra*) than on Dumas'; we therefore used small U-tubes charged with vitrioled pumice, such as we had used in our own syntheses. A current of hydrogen, purified by means of a tower of caustic soda and red-hot copper gauze, was passed through (1) a tube containing phosphoric anhydride; (2) a similar tube charged with the same reagent; (3, 4, and 5) three successive U-tubes charged with vitrioled pumice; and from the last vitriol tube the gas passed into the graduated Pisani.

Experiment I.—Volume of hydrogen used = 3.5 litres. Temperature = 17.5–17.8° C. The second P₂O₅-tube gained 0.1 m.grm., the three vitriol tubes

	(3)	(4)	(5)
Lost.. ..	0.3	1.6	4.8 m.grms.

Experiment II.—Volume of hydrogen used = 6 litres. Temperature = 16.5–17° C. The second P₂O₅-tube gained 2.3 m.grms., the three vitriol tubes

	(3)	(4)	(5)
Lost.. ..	0.3	1.0	0.0 m.grm.

Experiment III.—In this experiment a tube charged with recently-fused caustic potash was substituted for the first phosphoric acid tube. Volume of hydrogen used = 9.5 litres. Temperature not observed. The P₂O₅-tube gained 0.3 m.grm., the vitriol tubes

	(3)	(4)	(5)
Lost.. ..	1.2	1.9	–0.1 m.grm.

The tubes (3) and (4) correspond to the two vitriol tubes which were attached to our water-receptacle, and weighed before and after the synthesis. The conjoint loss of these two tubes in

Experiments	I.	II.	III.
was	1.9	1.3	3.1 m.grms.

The error, as we see, is not very considerable, but it is too great to be neglected, and with Dumas's very large U-tubes, it must have been greater than in our case. That the witness tube in Experiment I. lost almost 5 m.grms. is an anomaly which we cannot explain.

Of the several sources of error in Dumas's experiments,

* *Proceedings of the Philosophical Society of Glasgow.*

which we are able to see, only one remains to be considered. We allude to the unavoidable presence of *occluded hydrogen* in the metallic copper produced. Dumas was quite alive to this source of error, and, indeed, caused Melsens to determine its magnitude. In one of Melsens's experiments the metallic copper produced from 300 grms. of oxide by reduction hydrogen, when re-burned in oxygen, gave 65 m.grms. of water = 7.2 m.grms. of hydrogen or 0.000119 gm. per gm. of oxygen in the oxide of copper started with. Dumas states that once, when the reduction of the oxide was effected at an exceptionally low temperature, the copper contained 0.0002 of its weight of hydrogen. In this case the weight of hydrogen per gm. of oxygen in the original oxide was 0.0008 gm.

In the course of our first series of syntheses we sometimes determined the occluded hydrogen in the metal produced, and we may as well communicate the results now. After the completion of a synthesis of an evening, the reduction-tube was stopped up and kept over night. On the following morning the tube was re-weighed, to make sure that it had not changed weight, or to determine any change that might have taken place. It was then heated in a current of air, dried by means of vitrioled pumice, until it had suffered a very far-going oxidation, the water being collected in a tared U-tube charged with vitrioled pumice and weighed. In the following table the headings refer to the pages of our journal.

	Page—			
	44.	45.	67.	71.
Oxygen used as oxide of copper, grms. . . .	2.876	4.805	4.262	5.539
Water formed, in m.grms.	0.3	0.1	2.4	2.9
Occluded hydrogen . .	0.03	0.01	0.27	0.32
Hydrogen, per gm. of oxygen, m.grms. . .	0.1	0.002	0.0626	0.0582

	Page—			
	75.	77.	79.	89.
Oxygen used	10.372	10.526	10.424	15.460
Water produced . .	3.7	2.7	2.1	7.2
Occluded hydrogen . .	0.41	0.3	0.23	0.8
Ditto, per gm. of oxygen, m.grm. . .	0.0396	0.0284	0.0224	0.0518

Taking δ as a symbol for the occluded hydrogen per gm. of oxygen used apparently as oxide of copper, if the water obtained in the synthesis per 1 gm. of loss of weight suffered by the oxide of copper was $=k$, the true value k_0 of the ratio $H_2O : O$ is $k(1-\delta)$. Now, our highest value for $k\delta$ was 0.000071 gm., hence $k-k_0=0.000071$. Supposing, for instance, the true k_0 were equal to 1.125, then $k=1.125071$, corresponding for $O=16$, to $H=1.000568$.

But our average value for δ is only 0.0000344, hence $k-k_0=0.000039$, corresponding to $H=1.000312$. From Melsens's experiment with the metal from 300 grms. of oxide we should have $H=1.00100$. Our conclusion at the time was that the influence of the occluded hydrogen may safely be neglected.

To sum up :—Assuming Dumas's hydrogen contained the proportion of atmospheric oxygen corresponding to our determination V. (see p. 71), and 0.91 m.grm. of SO_2 per litre (see p. 91), then his (uncorrected) value $k=1.12547$ for $H_2O : O$ is liable to the following corrections :—

1. On account of the oxygen	—0.000287
2. On account of the sulphurous acid . .	—0.00154
Total	—0.001827

Hence, corrected value $k=1.12364$. All this on the assumption that the water-weights of Dumas are the *true weights*. If he forgot to reduce these to the vacuum, the corrected k must be corrected up by $0.001227 \times 1.12547 =$

0.00138, so that we have, for the fully corrected k' the number 1.12502; whence, for $O=16$, $H=1.00016$!

Let us now pass to a consideration of Erdmann and Marchand's work.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 2nd, 1893.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MR. WALTER H. INCE was formally admitted a Fellow of the Society.

Ordinary certificates were read for the first time in favour of Messrs. John Frederick Briggs, c/o Messrs. Parry and Co., Madras; Julian L. Baker, Stamford, Hendham Road, Upper Tooting, S.W.; William A. Bone, Schlossberg, 3, Heidelberg; H. W. Dickinson, Kent Place, Ulverston, Lancashire; John Addyman Gardner, 5, Bath Place, Oxford; John Alan Murray, 60, Marine Terrace, Aberystwyth; Alan E. Munby, 44, Holly Avenue, Newcastle-on-Tyne; J. Frank McGregory, M.A., Hamilton, N.Y., U.S.A.; James Henry Robbins, 4, Roderick Road, Haverstock Hill, N.W.; William Rintoul, 48, Carnarvon Street, Glasgow; George Rudd Thompson, 5, Clytha Square, Newport, Mon.

Of the following papers, those marked * were read :—

*106. "The Connection between the Atomic Weight of the Contained Metals and the Magnitude of the Angles of Crystals of Isomorphous Series." By ALFRED E. TUTTON, Assoc. R.C.S.

The author has subjected the crystals of twenty-two salts of the series of double sulphates $R_2M(SO_4)_2 \cdot 6H_2O$ containing as the alkali metal R potassium, rubidium, and caesium respectively, and as the second (dyad) metal M magnesium, zinc, iron, manganese, nickel, cobalt, copper, and cadmium respectively, to a detailed gonio-metrical investigation, with the purpose of ascertaining the nature of the connection specified in this title. The measurements have been made in great detail, at least 10 crystals of each salt, of the highest procurable degree of purity and perfection, selected from several different crops, having been completely measured: an average of over 400 measurements have thus been made in the case of each salt, 40 separate values of each of the principal angles being frequently obtained; this being considered necessary in view of the smallness of the differences under investigation, in order that on taking the mean of all the values of each angle the errors due to slight disturbances during deposition, and also the instrumental errors, might be eliminated. The purity of each salt was established by direct analysis. The twenty-two salts are fully described in the paper, and complete tables of their angles given. After each set of three salts containing the same second metal and potassium, rubidium, and caesium, respectively, as the alkali metal have been thus described, their angles are compared and the morphological relations are discussed.

The results of the investigation are embodied in the following summary :—

1. The salts containing caesium as the alkali metal are the most readily obtained in the form of crystals; those containing potassium the least; the salts containing rubidium occupying an intermediate position in this respect.

2. Though bounded by the same common planes, the crystals of the potassium, rubidium, and caesium salts of the series exhibit specific characteristic habits, the characteristic habit of the crystals of the potassium salts being widely different from that exhibited by the crystals

of the caesium salts, and the habit usually assumed by the crystals of the rubidium salts being of an intermediate character. The relations between the characteristic habits of the potassium, rubidium, and caesium salts respectively are thus found to be in direct correlation with the atomic weights of the alkali metals.

3. The axial angle β increases with the increase in the atomic weight of the alkali metal, its magnitude in any rubidium salt of the series being approximately midway between that in the potassium and that in the caesium salt containing the same second metal; in other words, the differences between the magnitudes of the axial angle in crystals of this series containing potassium, rubidium, and caesium respectively as the alkali metal are in direct simple proportion to the differences between the atomic weights of these metals.

The changes in the magnitude of the axial angle on passing from a potassium to a rubidium salt, and from a rubidium to a caesium salt, are very considerable, usually exceeding a whole degree in each case; they are therefore far outside the limits of possible experimental or formational error.

4. The magnitudes of all the angles between the faces of the crystals of the salts of this series containing rubidium as the alkali metal lie between the magnitudes of the corresponding angles upon the crystals of the salts containing potassium and caesium respectively.

The differences between the magnitudes of the angles other than the axial angle, in crystals of this series containing potassium, rubidium, and caesium respectively as the alkali metal are not generally in direct simple proportion to the differences between the atomic weights of these metals. The maximum deviation from simple proportionality occurs in the prism zone, in which the ratio of the difference varies, according to the nature of the second metal present, from 1:2 to 1:3.

The fact that the differences between the magnitudes of many of the angles of the caesium and rubidium salts are so much larger than those between the rubidium and potassium salts would appear to indicate that as the atomic weight increases, it exercises an influence on these angles in excess of the mere numerical proportion to its increase. This influence is most apparent in the case of the angles of the prism zone, and becomes less and less evident in the zones approaching more and more nearly to the plane of symmetry, until at length, in the case of the axial angle lying in the plane of symmetry, all evidence of it disappears, and the differences are then directly proportional to the numerical differences in atomic weight.

5. The alkali metals exert a preponderating influence in determining the geometrical form of the crystals, the magnitudes of the angles being altered on displacing one alkali metal R by the next higher or lower to an extent attaining a maximum in certain angles of more than a whole degree, while the displacement of the second (dyad) metal M by any other of the same group is unattended by any material change in the angular magnitudes.

6. The importance of the axial ratios as indicative of the change of geometrical form on displacing one alkali metal in any salt of the series by another is greatly diminished by the fact that simultaneous changes more or less neutralising each other occur in the angles which determine them, thus causing the differences to be small. It is generally observed, however, that in any set of three salts containing the same second metal the ratios in the case of the rubidium salt lie between those of the potassium and caesium salts, and somewhat nearer to those of the potassium salt. The changes in the angles themselves afford the only complete information concerning the change in geometrical form.

The optical properties of the crystals of the salts now considered will be described and discussed in a subsequent communication.

DISCUSSION.

Mr. MIERS remarked that Mr. Tutton appeared to attribute the intermediate position occupied by the

rubidium sulphates to the fact that the atomic weight of rubidium is the arithmetic mean of those of potassium and caesium; if this were the simple cause, we should expect similar relations to obtain in the lithium, sodium, and potassium, or the calcium, strontium, and barium series, or in the case of an homologous series of hydrocarbon radicles. The strontium salts, however, are not intermediate in form between those of barium and calcium in the case of the bromates, the sulphates, or the carbonates, and even in the potassium-rubidium-caesium series the platinonitrites and the platiniodonitrites prepared by Nilson afford results showing that the rubidium salt does not necessarily occupy an intermediate position. Hence it is impossible at present to draw simple general conclusions from the results afforded by these or other isomorphous series, as the relations obtaining in one series do not generally prevail in others. Mr. Miers expressed the hope that Mr. Tutton would extend his observations to the isomorphous selenates.

*107. "The Preparation of Phosphoric Oxide free from the Lower Oxide." By W. A. SHENSTONE and C. R. BECK.

A description is given of a method of preparing phosphoric oxide free from the lower oxides by distilling it over platinum sponge in the presence of excess of oxygen. The authors refer to a similar process lately described by Professor Threlfall (*Phil. Mag.*, January, 1893), and call attention to certain points in this process which in their experience considerably improve its efficiency and value.

DISCUSSION.

Professor THORPE, referring to the strictures passed on the commercial phosphoric oxide by Mr. Shenstone, said that in his experience it was by no means unsatisfactory in quality. Mr. Tutton and he had failed in extracting more than a minute proportion of phosphorous oxide from it.

Mr. H. B. BAKER agreed with Professor Thorpe; he had been in the habit of testing for the tetroxide by means of carbon tetrachloride, which dissolves it but not phosphoric oxide.

Mr. SHENSTONE, in reply, said he had not intended to imply more than that the commercial product was impure; the percentage of impurity was probably small.

*108. "Contributions to our Knowledge of the Aconite Alkaloids. Part IV. On *Isaconitine* (*Napelline*)." By WYNDHAM R. DUNSTAN and E. F. HARRISON.

The authors have investigated the nature and properties of the alkaloid found together with aconitine in the roots of *Aconitum napellus* (see Part II.), to which it was proposed to assign the old disused name of napelline; this alkaloid always occurs in the roots to as large an extent as aconitine and in some cases to a larger extent. The preparation of the pure substance is fully described in the paper. Its separation from aconitine is based on the superior solubility of the latter in ether, while its superior solubility in chloroform affords a means of separating it in greater part from the other associated alkaloids; it is finally purified by re-crystallising its hydrochloride. It is found to be *isomeric* with aconitine, and the name *isaconitine* is therefore now adopted instead of napelline, to which objections were raised on a former occasion.

Isaconitine has hitherto always been obtained in a colourless friable varnish-like form, resisting all attempts to crystallise it; it is readily dissolved by alcohol and chloroform, less readily by ether, and it is only slightly soluble in water, though more so than aconitine. The alcoholic solution is feebly dextro-rotatory.

The hydrochloride, $C_{33}H_{45}NO_{12} \cdot HCl$, crystallises from water in rosettes soluble in alcohol, containing 1 mol. prop. of water. The aqueous solution is intensely bitter, and is lævo-rotatory to almost the same extent as the aconitine salt, $[\alpha]_D = -28.74^\circ$.

The corresponding hydrobromide and hydriodide form similar crystals, but are anhydrous; the latter salt is

laevorotatory, $[\alpha]_D = -26.94^\circ$. All these compounds somewhat resemble the corresponding aconitine salts in their physical properties.

Isaconitine exhibits a remarkable behaviour with auric chloride which sharply distinguishes it from aconitine, and, indeed, from most other alkaloids. Hitherto no definite *aurichloride* has been obtained, but it is found that when solutions of the hydrochloride and of auric chloride are mixed, a yellow amorphous precipitate is produced as in the case of aconitine; on re-crystallising this from alcohol, nearly colourless crystals are obtained of an *aurochlorisaconitine*, of the formula—



This is apparently a derivative of the alkaloid in which one atom of hydrogen is displaced by the group $AuCl_2$. The first known alkaloidal derivative of this type, namely, *aurochlorcaffeine*, was described a short time ago by Dunstan and Shephard (*cf. Trans.*, Feb., 1893). The production of such a compound from napelline was altogether unexpected. *Aurochlorisaconitine* differs, however, from *aurochlorcaffeine* in not being re-converted into the *aurochloride* by the action of hydrogen chloride.

When isaconitine is heated either with water in closed tubes or under ordinary pressure with mineral acids, it is gradually hydrolysed. The hydrolysis is more rapidly effected by aqueous solutions of soda or potash, which act even in the cold. It yields the same products as aconitine and the same proportions, viz., aconine and benzoic acid, $C_{33}H_{45}NO_{12} + H_2O = C_{26}H_{41}NO_{11} + C_7H_6O_2$.

The physiological action of isaconitine has been compared with that of aconitine by Professor Cash, who finds that the action of the two alkaloids is entirely distinct. A solution of a pure isaconitine salt does not produce the tingling sensation on the tongue which is so characteristic of aconitine; and while aconitine is a most violent poison, even in excessively minute doses, relatively considerable quantities of isaconitine must be administered to small animals in order to produce a toxic effect, which effect is the result of a physiological action in the main distinct from that of aconitine. It seems doubtful whether isaconitine would prove toxic to man, except when given in very large doses.

It may be added that the new alkaloid now described under the name of isaconitine is entirely different from the mixtures of amorphous alkaloids called napelline by the earlier workers. It also differs in composition and properties from the picraconitine of Wright, and the amorphous bases since obtained from the roots of *Aconitum napellus* by other investigators. Having regard to the manner in which these amorphous bases were prepared, and to the extreme difficulty which is experienced in preparing pure isaconitine, it may be safely concluded that they were not single substances.

*109. "Contributions to our Knowledge of the Aconite Alkaloids. Part V. The Composition of some Commercial Specimens of Aconitine." By WYNDHAM R. DUNSTAN and FRANCIS H. CARR.

The authors have examined a number of English and foreign specimens of aconitine. For several of these they are indebted to Dr. J. W. L. Thudichum, who collected them some years ago; others have been purchased during the last two years. Dr. Thudichum had found that the various specimens differed enormously in their toxic power, many being nearly inert, while a few were highly poisonous.

The process used in examining these "aconitines" was essentially that described in the preceding communication, by means of which aconitine, isaconitine, homisaconitine (homonapelline), and aconine could be isolated, and the quantity of each approximately determined. The method of estimating aconitine first proposed by Wright, and recently advocated in a slightly modified form by Allen, in which the benzoic acid produced on hydrolysis of the mixture of alkaloids is reckoned as derived from aconitine, is valueless, since isaconitine

furnishes benzoic acid in the same proportion as aconitine when hydrolysed. Sixteen specimens of "aconitine from *A. napellus*" and its salts were examined. Most of the samples were amorphous; these were invariably found to contain but a very small proportion of aconitine, in some cases none, but were chiefly composed of the amorphous alkaloids aconine, isaconitine, and homisaconitine, all of which appear to be very slightly, if at all, toxic. It would seem that, as a rule, "amorphous aconitine" represents the total alkaloids of the root. Of the crystalline specimens of alkaloid only two were pure, most of them being contaminated with more or less amorphous alkaloid. The specimens of aconitine salts examined were found, in nearly every case, to be chiefly isaconitine salts containing only small quantities of aconitine compounds. Hence it is not surprising that great differences have been observed in the mode of action and toxic power of commercial "aconitine." It is most important that in future nothing but pure crystalline aconitine possessing the characters fully described in Part I. of the enquiry should be used in medicine, and it is satisfactory that a pure alkaloid can now be obtained in commerce.

DISCUSSION.

Mr. HOWARD characterised the discovery of the extraordinary difference between aconitine and the isaconitine now described as a striking example of the value of high "theoretical" chemistry; the discovery of the explanation of the difference would be of the deepest interest.

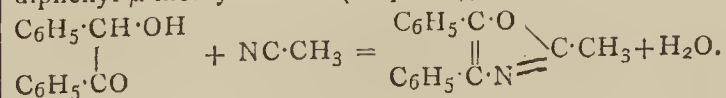
Dr. STEVENSON, after alluding to the impure nature of German commercial aconitine, dwelt on the importance of using crystallised material, which gave fairly constant results; such was the virulence of the alkaloid that $2/1,000$ ths of a grain never failed to kill a large mouse, and 3 m.grms. usually proved fatal to an adult man.

Dr. BRUNTON spoke of the fear of prescribing "aconitine" which existed owing to its irregular character; in the course of experiments made twenty-two years ago, he had himself obtained most conflicting results, having, doubtless, used different "aconitines." He then remarked on the scientific interest attaching to the determination of the nature of the alkaloidal constituents of the various species of aconite, and the light which might thereby be shed on the origin of the different alkaloids: *A. heterophyllum*, unlike most species, contained no poisonous principle, and it would be specially interesting to examine this.

Professor DUNSTAN, in reply, said that German aconitines were not all amorphous and valueless; moreover, it was a mistake to suppose that a sample was pure because it was crystalline. *A. heterophyllum*, to which Dr. Brunton had alluded, had a very bitter taste; as this was characteristic of isaconitine, perhaps this alkaloid was present.

110. "Synthesis of Oxazoles from Benzoin and Nitriles." By FRANCIS R. JAPP, F.R.S., and T. S. MURRAY, D.Sc.

The authors find that nitriles and benzoin interact when a mixture of the two compounds is dissolved in concentrated sulphuric acid, water being eliminated, an oxazole being formed in which the hydrocarbon radicle attached to the cyanogen of the nitrile occupies the *meso*-position, e.g., in the case of acetonitrile, which yields $\alpha\beta$ -diphenyl- μ -methyloxazole (m. p. 28°),—



In addition to the foregoing, they have prepared $\alpha\beta$ -diphenyloxazole, $C_{15}H_{11}NO$ (m. p. 44°), from benzoin and hydrogen cyanide; $\alpha\beta$ -diphenyl- μ -ethyloxazole, $C_{17}H_{15}NO$ (m. p. 32°), from benzoin and propionitrile; and triphenyloxazole, $C_{21}H_{15}NO$ (m. p. 115°), from benzoin and benzonitrile. Triphenyloxazole is identical with Laurent's *benzilam* and Zinin's *azobenzil*.

By heating $\alpha\beta$ -diphenyl- μ -methyloxazole with ammonia, it is converted into the corresponding imidazole, identical with Japp and Wynne's methyldiphenylglyoxaline, the oxygen atom in the ring being displaced by NH.

III. "The Action of Nitrosyl Chloride and of Nitric Peroxide on some Members of the Olefine Series." By WILLIAM A. TILDEN and J. J. SUDBOROUGH.

The authors have examined the action of nitrosyl chloride on the first five members of the olefine series with the following results:—Ethylene forms only the dichloride; propylene and butylene a mixture of dichloride and nitroschloride, while trimethylene (amylene) is almost entirely converted into a nitroschloride. Phenylethylene (cinnamene) behaves like trimethylethylene. Further, it is now found that propylene affords a compound similar to that prepared by Guthrie many years ago from nitric peroxide and amylene. The study of these compounds has been undertaken with the view of elucidating the constitution of the nitroschlorides formed by the terpenes.

II2. "Piperazine." By W. MAJERT and A. SCHMIDT.

Erroneous statements have appeared in several modern text-books regarding the physical and chemical characters of piperazine, $C_4H_{10}N_2$, which have been confused with those ascribed by A. W. von Hofmann and by Ladenburg to the impure substances of like composition discovered by them, and termed respectively diethylenediamine and ethyleneimine or diethylenedimine; our attention has been directed to the fact that this misunderstanding has partly arisen from a misconstruction of our views (*Ber.*, 1890, 3719) as to the identity of these substances: we, therefore, desire to correct this impression.

Piperazine, which was not known in its pure crystalline condition until prepared by us in August, 1890, by treatment of dinitrosodiphenylpiperazine with alkali, is a crystalline substance melting at $104-107^\circ$ in capillary tubes, although when the melting point is determined on large quantities it is found to be 112° , the differences being due to the hygroscopic nature of the base; it boils at $140-145^\circ$. It is very readily soluble in water and alcohol, the aqueous solution having a distinctly alkaline action. It is very hygroscopic and readily absorbs carbon dioxide, being thereby converted into the carbonate melting at $162-165^\circ$.

Piperazine is especially characterised by the formation of an insoluble pomegranate-red double salt with bismuth iodide and by a dibenzoyl compound melting at 191° .

The basic substance diethylenediamine prepared by Hofmann by the interaction of ammonia and ethylene bromide consisted of a liquid mixture of bases boiling approximately at 170° . That this mixture contained a small quantity of a base identical with piperazine is undoubted, but it was only after piperazine had been prepared from dinitrosodiphenylpiperazine that Hofmann succeeded in identifying it and isolating the pure crystalline product from the mixture, which, besides higher ethylene bases, contained also a number of vinyl compounds.

Owing to the difficulty of purifying small quantities of the base, Ladenburg's experiments with diethylenedimine, obtained by the decomposition by heat of ethylenediamine hydrochloride, were unsuccessful: the product described by Ladenburg as the base was undoubtedly impure piperazine carbonate, as proved by its melting point, $159-163^\circ$.

In conclusion, it may be interesting to mention that we have succeeded in preparing the following series of hydrates of piperazine, that most readily formed being a hexhydrate which crystallises from dilute aqueous solutions:—

$C_4H_{10}N_2 \cdot H_2O$, m. p.	75° ,
" $2H_2O$, "	56° ,
" $3H_2O$, "	$39-40^\circ$,
" $4H_2O$, "	$42-43^\circ$,
" $5H_2O$, "	45° ,
" $6H_2O$, "	48° ,

NOTICES OF BOOKS.

An Introductory Manual for Sugar-Growers. By FRANCIS WATTS, F.C.S., F.I.C., Associate Mason College, Birmingham, and Government Chemist, Antigua. London and New York: Longmans, Green, and Co., 1893. Crown 8vo., pp. 151.

THIS work is an able attempt at the correction of one of our national sins of neglect. Any other Empire including such an extent of tropical and semi-tropical territories as does that of Her Majesty would long ago have made the cultivation of crops suitable for such climates the subject of the most careful and persistent experiment and study, and have distributed the information so gained among the colonists or those likely to become such. We, until lately at least, have been content to turn swine, sheep, oxen, and, *proh pudor*, goats, into the most fruitful lands. When foreigners have devised some product to compete with tropical crops, we have let judgment go against us, so to say, by default. Of this neglect a striking instance occurs in the very product discussed in the work before us. Beet-sugar, it is well known, was one of the weapons forged against us by perhaps the most astute and powerful of our enemies, and even yet it is diligently wielded against us.

We are, therefore, exceedingly glad to find Mr. Watts coming forward to instruct our planters in the scientific principles of agriculture as applicable in tropical climates. It is sad to see farmers skilled in all the mechanical routine of husbandry going out to the Colonies and either working in a quite unsuitable manner or seeking to grow crops which require cold and damp air and soils.

Mr. Watts expounds the rudiments of agricultural chemistry and vegetable physiology in a plain, intelligible manner. Thus, in the first chapter we have an account of plant cells, tissues, and fibro-vascular bundles, of the structure and function of roots, stems, and leaves. The second chapter introduces us to the components of soils, to the conditions affecting fertility, to nitrification, the action of leguminous crops in the fixation of nitrogen. Chapter III. deals specially with the sugar-cane, whilst Chapter IV. discusses manures. Here green-dressing—the ploughing in of certain green crops—is recommended as a source of nitrogen and as improving the condition of the soil, but the inability of farmyard manure alone to maintain fertility is fully admitted. Manures for the West Indies should always be of a concentrated character to economise freight. Basic slag is recommended as deserving more attention than it has hitherto received. The use of ferrous sulphate seems to have given favourable results in some experiments instituted by the author.

The fifth, sixth, and seventh chapters treat of the manufacture of sugar in its different stages. The relative advantages and disadvantages of diffusion as compared with crushing are discussed, the author considering that the success of the former process in the West Indies is problematical.

The eighth chapter speaks of hydrometers and their use. We regret to find that the planters still cling to Beaumé's instrument, which not only does not admit of ready re-calculation into direct specific gravity and weight per gallon, but exists in two, if not three, discrepant forms. If they would use Twaddell's hydrometer they could not fail to become convinced of its superiority.

The ninth chapter deals with the utilisation of molasses. Various processes applicable to beet molasses are useless for the product of the cane. The author does not bring into sufficient prominence the fact that beet molasses is unfit for human consumption. But as a general rule he recommends distillation, *i.e.*, the production of rum. This outlet has, however, been lessened by the circumstance that rum is now largely adulterated with grain-spirits and even with potato-whiskey.

We think that in this excellent work some reference

might have been advantageously made to the practical researches of Prof. R. Galloway. The only error we can discover is that the atomic weight of platinum is still given as higher than that of gold. As a whole, Mr. Watts's treatise deserves warm approval and extensive study.

Physics: Advanced Course. By GEORGE F. BARKER, Professor of Physics in the University of Pennsylvania. London: Macmillan and Co., 1892.

ANY man who had studied physics a quarter of a century ago and had not kept up the subject, would find himself no little perplexed on opening this volume. It is not so much that he will encounter novel facts and new generalisations—though in the meantime important discoveries have certainly been made—as that admitted truths are viewed in a new light. The author defines physics as the science of energy, whilst chemistry he thinks may be regarded as the science of matter.

To this second definition exception may fairly be taken. Were there only one kind of matter within our reach, where would be our chemistry? At the same time this one kind of matter would have certain properties,—commonly known as its mechanical properties,—which might be a legitimate object of study.

After introductory considerations the author divides his subject into mass physics, molecular physics, and physics of the ether. The phenomena of sound are discussed in the first section as "energy of mass-vibration."

The laws of heat fall under the head of molecular physics, along with its transference, its sources, and thermo-chemistry. It is doubtful whether any of the theories of the origin of solar energy can be accepted in face of the results to which they lead. The view of the late Sir W. Siemens, as to the recuperation of the sun's heat, is not discussed.

The fourth part takes up the physics of the ether, commencing with the energy of ether vibration or radiant energy, commonly known as light. The characteristics of the ether are given with the necessary proviso that it is known only by its properties. The interesting fact is mentioned that while only 2·4 per cent of luminous waves are present in the radiation from a gas-burner, 10 per cent in that of an arc-light, and only 35 per cent in that of the sun, the radiations of the fire-fly (*Pyrophorus noctilus*) are wholly composed of visible wave-lengths. Here, therefore, is a field for the inventor!

It is shown by the researches of Prof. Langley that the temperature of the earth depends less on the direct solar heat than on the quality of selective absorption of the atmosphere.

The principles of photography, the radiometer, and the radiophone are next described, though without any new revelations.

The dark lines in the solar spectrum and the spectro-scope in its various uses, chemical and astronomical, are expounded. The colour sensation and colour blindness are made the subject of a careful investigation.

Next follows the energy of ether-stress (electrostatics), the energy of ether-vortices (magnetism), and the energy of ether-flow (electrokinetics).

In a concluding chapter follow the relations between light and electricity, and the electro-magnetic theory of light. Maxwell's electro-magnetic theory of light is considered as based upon a firm foundation of experimental fact.

We can scarcely hesitate to pronounce this work the best truly modern manual of physics in our language.

The Year Book of Science. Edited for 1892 by Prof. T. G. BONNEY, D.Sc., LL.D., F.R.S. London, Paris, and Melbourne: Cassell and Co., Limited, 1893.

So rapid is the advance in these days of the sciences, and so much is the individualisation of each increased, that a work of this kind is needful, not merely for the

general reader, but even for specialists themselves, who, immersed each in his own department, are in danger of forfeiting the *esprit d'ensemble*. The object of the editor and his contributors has been to give a condensed view of the progress effected in each department. All the physical and natural sciences are duly considered. The subjects omitted would have been somewhat out of place. Statistics, for instance, is not, strictly speaking, a science, but a method applicable in various sciences; mathematics, in its higher developments, cannot be made interesting to the non-mathematician, and "economy" has not yet reached its scientific stage.

The subject-matter has been selected from trustworthy sources, from the Transactions of Societies of good standing, or from the works of eminent authors. One section only, that on organic chemistry, will be obscure, save to organic chemists themselves.

It may, perhaps, surprise us to find the important subject of bacteriology placed under the head of animal biology, since these ultra-minute beings are now generally regarded as microphytes.

Mr. Thomas Hick, B.Sc., is responsible for a new and, we think, rather needless term "palæobotany."

In the distribution of space chemistry fares well, as it occupies eighty-six pages, of which fifty fall to the lot of organic chemistry. General physics occupies one hundred and thirty-four pages, of which sixty pages are taken up with the popular subject of electricity.

To the biological (animal) section, eighty pages have been assigned, and of this space only four fall to the lot of insects. This is very little if we consider that they are more numerous in species than all the other organic forms taken collectively, and that they exert a most important influence on the life and well-being of mankind.

Experiments made in the hope of rendering animals "immune" to the venom of the cobra by successive inoculation with minute doses have so far not proved successful. Neither has the strychnine treatment.

The "Year Book of Science" ought to be in the library of every man who wishes to remain intellectually on a level with the age.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—Allow me to assure Mr. Keyworth that no resolution has been passed by the Institute of Chemistry to erase the letters F.C.S. from the Register; such a resolution was proposed, but was not carried.

The resolution adopted was to the effect that *all* letters should be erased after the name of a Fellow excepting those indicating a Degree or Fellowship of the Royal Society, London. As far as I understand my own language the two resolutions are totally different, and how anyone can maintain that they are identical either in effect or intention passes my comprehension.—I am, &c.,

F. J. M. PAGE.

Chemical Laboratory, London Hospital, E.,
February 26, 1893.

Mercuric Chloride as a Reagent for Albumen in Urine.—E. Spiegler (*Berichte*).—This reagent is rendered more sensitive if applied in the state of a solution of 8 grms. sublimate, 4 grms. tartaric acid, and 20 grms. sugar in 200 c.c. water. If albuminous urine is slightly acidified with concentrated acetic acid and super-stratified upon the reagent, which is specifically heavier, there is formed a sharp whitish ring at the plane of contact. The test is even more sensitive than the ferrocyanide reaction. It is not affected by urinary peptone.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 7, February 13, 1893.

Study of the Meteorite of the Cañon Diablo.—Henri Moissan.—The fragments of the meteorite which the author has examined contain transparent diamond, black or carbonado, and a maroon-coloured carbon of very low specific gravity. In certain fragments he has been able to show the presence of graphite in the form of small masses of a fatty aspect. Transparent diamond may therefore be found in other planets besides the earth.

Meteoric Iron of the Cañon Diablo.—C. Friedel.—The author has obtained from this meteorite an iron sub-sulphide, Fe_5S , as a brilliant compound, less attackable by acids than iron. There is also a small quantity of a phosphide which has not yet been determined. There occur also nodules of yellow troilite.

Presence of Graphite, Carbonado, and Microscopic Diamonds in the "Blue Earth" from the Cape.—Henri Moissan.—The pits in which the South African diamonds are found are filled with a serpentinous breccia containing more than eighty species of minerals, and not containing per cubic metre more than 500 m.grms. of crystalline carbon. The matter of a specific gravity exceeding 3.4 is composed of an amber yellow matter in irregular masses, of carbonado or black diamond, of microscopic diamonds, and of small transparent crystals which do not burn in oxygen, which take the form of elongated prisms, and which do not fluoresce in violet light. The yellow matter contains much iron and has been recognised also in bars of cast iron. The transparent crystals consist chiefly of silica.

Action of Temperature on the Rotatory Power of Liquids.—Albert Colson.—The author's experiments show that physical causes may alter the rotatory power of liquids to a considerable extent, even giving rise to changes of sign, and that the chemical constitution does not seem to be the preponderating factor in the value or in the sign of the rotatory power.

Considerations on the Genesis of the Diamond.—J. Werth.—The author concludes that the diamond has been formed at a high temperature and under pressure. When formed it has been cooled rapidly. It has been formed in presence of hydrogen more or less carburetted.

Chlorine Derivatives of the Propylamines, Benzyl amines, Aniline, and Paratoluidine.—A. Berg.—The author obtains these derivatives by the method which enabled him to prepare those of the amylamines and isobutylamines. He has prepared and examined propylchloramine, propyldichloramine, dipropylchloramine, benzylchloramine, benzyldichloramine, dibenzylchloramine, and certain chloroderivatives of aniline and paratoluidine.

Dipropylcyanamide and Dipropylcarbodiimide.—F. Chancel.—The contents of this paper are sufficiently shown by the title.

Zeitschrift für Analytische Chemie.
Vol. xxxii., Part 1.

Detection of Glucose in the Blood.—Pickardt (*Zeit. Phys. Chemie*).—The blood is first freed from albumen and colouring-matter by means of zinc acetate and strongly concentrated. By means of phenylhydrazin and sodium acetate crystals are obtained, which exactly agree with the corresponding compound of glucose.

Examination of Metallic Iron for Arsenic.—Otto Sautermeister (*Chem. Zeit.*).—Arsenious acid may be added to 1 grm. of the iron to the extent of 1 decigram.

without giving an arsenical mirror by the Marsh process. An arsenic reaction was obtained in the filtrate with Bettendorff's test (stannous chloride), but not if the filtration is effected after the development of hydrogen has ceased.

Separation of Toxaalbumines.—Konrad Alt has separated a toxaalbumen from the matter vomited by cholera patients. The clear liquids are precipitated with alcohol.

The Atomic Weight of Cadmium.—W. L. Lorimer and E. F. Smith.—Already inserted.

MEETINGS FOR THE WEEK.

- MONDAY, 6th.—Medical, 8.30. (General Meeting).
 Society of Arts, 8. "Alloys," by Prof. W. Chandler Roberts-Austen, C.B., F.R.S. (Cantor Lectures).
 Royal Institution, 5. General Monthly Meeting.
 Society of Chemical Industry, 8. "A Convenient Form of Experimental Apparatus for Filtrations and other Determinations," by C. C. Hutchinson. "The Composition of the Petroleum-like Bitumen of Japanese Coal," by Mr. Watson Smith. "The Detection and Estimation of Lead in Citric and Tartaric Acids," by Mr. Warrington.
- TUESDAY, 7th.—Institute of Civil Engineers, 8.
 Pathological, 8.30.
 Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psychophysiology," by Prof. Victor Horsley, F.R.S.
- WEDNESDAY, 8th.—Society of Arts, 8. "Music in Elementary Schools," by W. G. McNaught.
 Medical, 8.30. (Annual Dinner).
 Geological, 8.
 Pharmaceutical, 8.
- THURSDAY, 9th.—Royal, 4.30.
 Royal Institution, 3. "The Great Revival—A Study in Mediæval History," by the Rev. Augustus Jessopp, D.D.
 Society of Arts, 8. "Caste and Occupation at the Last Census of India," by Jervoise Athelstane Baines, I.C.S.
 Institute of Electrical Engineers, 8.
 Mathematical, 8.
- FRIDAY, 10th.—Royal Institution, 9. "Early Myth and Late Romance," by Sir Herbert Maxwell, M.P.
 Astronomical, 8.
 Physical, 5. "The Application of Lagrange's Equations of Motion, with especial Reference to a Perforated Solid in a Liquid," by Dr. C. V. Burton. "On the Magnetic Field of a Circular Current," by Prof. G. M. Minchin, M.A. "On the Differential Equation of Electrical Flow," by T. H. Blakesley, M.A.
- SATURDAY, 11th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Books.—What books would you advise a young chemist to take with him on going out to the gold mines in South Africa?—ONWARD.

Filters.—I am desirous of information, for lecture purposes, on the subject of filters, and should feel obliged if readers of the CHEMICAL NEWS would tell me where details and diagrams on this subject are to be found.—WATER.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1737.

ON THE ORIGIN OF COLOUR.

III. IODINE AND IODINE SOLUTIONS.

By WILLIAM ACKROYD.

(Continued from p. 653)

THE element iodine under the influence of heat forms an exception to the rule followed by the bodies so far considered, and its colour scale may prove of use in the study of the class of compounds with isolated absorption-bands. Yellow to reddish brown in thin film it becomes violet on being converted into the vapourous state, and it has two classes of solutions, apparently corresponding to these two states, viz., yellow solutions when the solvent is alcohol or aqueous potassium iodide, &c., and violet solutions when CS_2 or CCl_4 and certain other bodies are the solvents. I have attempted to make quantitative comparisons between yellow solutions and the solid, and between violet solutions and the gas.

To compare the spectra of a given number of gaseous molecules of iodine with the same number in CS_2 solution the following method was adopted. Into small flasks of about 85 c.c. capacity a few grains of iodine were introduced and vapourised in an air-bath with parallel glass sides. The spectrum yielded by one of these being noted for various temperatures, the neck which had been previously drawn out to a capillary tube was now sealed at about 110°C . After removing the flask and allowing the iodine to solidify, the tip of the neck was broken off and the flask filled with re-distilled CS_2 . All the iodine was now in solution which before existed as vapour, and the light passing through the same parts of the flask on its way to the spectroscope was necessarily acted on by the same number of molecules. With the gaseous iodine there was first observed faint dark lines in the green and yellow. As the quantity of vapour increased there appeared (1) three faint absorption-bands, whose approximate positions in tenth metres I make to be 5456, 5246, and 5047; (2) increase in number of the faint dark lines towards the red, and merging of bands 5047 and 5246 into one. This same quantity of iodine dissolved in CS_2 gave one band covering the three gaseous bands, and minus the faint dark lines, its general position being moved a little more towards the violet end of the spectrum than that of the gaseous iodine spectrum.

Now in this case an eye observation notes a change from *red* solid or liquid film to *violet* gas. This iodine colour scale cannot be well introduced into the one we have so far used, as in assuming a violet colour iodine exhibits a distinct line of divergence from the usual order. The element may in this be to some extent typical of a few other bodies, as, for example, some of the organic compounds to which it exhibits points of resemblance, as in dissolving in organic solvents and forming two classes of solutions. It is to some such scale that the rosaniline compounds conform, thus:—

Rosaniline Red, $\text{C}_{20}\text{H}_{19}\text{N}_3$.
Phenylrosaniline .. Red violet, $\text{C}_{20}\text{H}_{18}(\text{C}_6\text{H}_5)\text{N}_3$.
Diphenylrosaniline .. Blue violet, $\text{C}_{20}\text{H}_{17}(\text{C}_6\text{H}_5)_2\text{N}_3$.
Triphenylrosaniline .. Blue, $\text{C}_{20}\text{H}_{16}(\text{C}_6\text{H}_5)_3\text{N}_3$.

In passing, one may be permitted to suggest that exact conformity to any scale is not likely to be always observed, as there may possibly be risings and fallings in the colour scale analogous to the rise and fall of melting-points in certain homologous series.

I have made quantitative observations of violet solutions of iodine by the method I described in 1877 (CHEM.

NEWS, vol. xxxvi., p. 159), and constructed diagrams where the ordinates are lengths of the solution in c.m. looked through, and the abscissæ are the spectroscopic readings or their equivalents in wave-lengths. Fig. 1 is

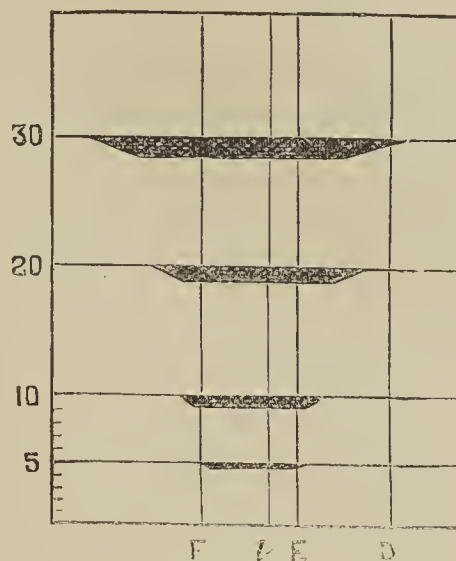


FIG. 1.—Violet solutions.
(0.00004 grm. I per c.c.).

the diagram obtained for iodine dissolved in CCl_4 or CS_2 to the extent of 0.00004 grm. per c.c. With 5 c.m. of either of these solutions the green portion of the spectrum appears of decreased intensity, but without any decided band; and this may be put down as the commencement of the absorption. Light passing through 30 c.m. gives a band extending up to D on the one hand, and beyond F on the other with hazy borders. The point of interest which is demonstrated by this quantitative comparison is that the chemical difference of constitution in the two solvents has evidently no tendency to produce differences in the nature or extent of the light absorbed.

It is self-evident that violet solutions of iodine cannot conform to the law of constancy of absorption as set forth in my paper on "Transverse Absorption of Light" (CHEM.

NEWS, vol. xxxvi., p. 159). The formula $\frac{cs}{m} = t$ may,

however, be used for finding the thickness of solid iodine corresponding to the quantity, producing incipient absorption in violet solutions, where c = stratum, length of

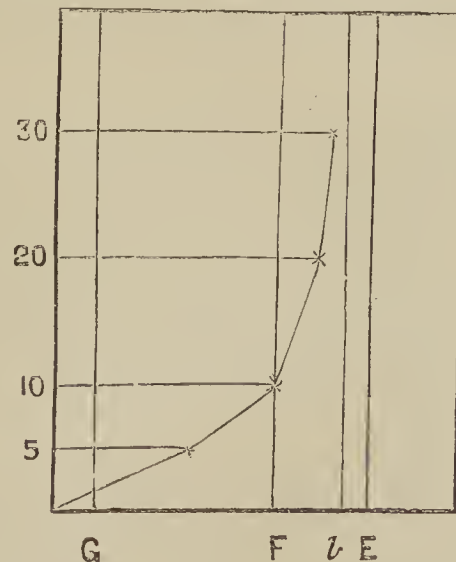


FIG. 2.—Brown solution of iodine.
(0.00062 grm. per c.c.).

solution in c.m.; s = strength in grms. per c.c.; m = weight in grms. of 1 square c.m. of solid, 1 m.m. in thickness; and t = thickness of solid plate in m.m. In the case in point we have the commencement of absorp-

tion in violet solutions with a quantity of iodine equal to a film of solid—

$$\frac{5 \times 0.00004}{0.4948} = 0.0004 \text{ m.m.,}$$

or 4000 tenth-metres thick, which is within the range of the limits of the wave-lengths of light.

As representative of the class of yellow to brown solutions, Fig. 2 gives the curve obtained for a solution of iodine in alcohol containing 0.000062 gm. of the element per c.c. Here the violet end of the spectrum is absorbed, and the absorption increases until, with 30 c.m. of solution, *b* is nearly reached. The thickness of solid film equivalent to the amount of iodine producing absorption up to *F* is—

$$\frac{10 \times 0.000062}{0.4948} = 0.0012 \text{ m.m.,}$$

or 12,000 tenth-metres. This figure is a close approximation to Sir John Conroy's estimate, made by other methods, of the thickness of films of iodine, varying in colour from deep brownish-red to brown ("The Absorption Spectra of Iodine," *Phil. Trans.*, vol. xxv., p. 51 *et seq.*).

The foregoing comparisons lead me to place the various appearances of iodine and its solutions in the following order of evolution:—

1. Yellow to brown .. Solid and liquid films.
2. " " .. Solutions in alcohol, &c.
3. Violet .. Solution in CS₂, &c., one absorption band.
4. Violet .. Vapourous iodine, three absorption-bands + fine lines.

As one may regard this order of change as being in large part due to disintegration of molecular masses, I have made an attempt to find out the relative amounts of heat absorbed due to solution, but so far unsuccessfully, this being owing to the fact of so small an amount of iodine being dissolved that an error of a tenth of a degree C. rendered the results entirely valueless.

Halifax, Feb. 20, 1893:

ACTION OF CARBON UPON SOLUTIONS OF SALTS OF THE RARE EARTHS.

By K. HOFMANN and G. KRÜSS.

Porous carbon, especially bone-black, is well known to possess the power of absorbing certain substances whether from the air or from a solution into which it is introduced. In most cases this depends upon the fact that the surface attraction here reaches a perceptible degree of efficacy in consequence of the great extension of surface, although no chemical process occurs. But in other cases, chemical reactions may be recognised. Thus, *e.g.*, porous charcoal partially precipitates on its surface hydroxides from the saline solutions of feebly basic oxides such as those of iron and aluminium, whilst free acid is split off.

Accordingly we examined whether the behaviour of the rare earths was similar to that of the oxides just named, and whether the weaker earths are not liable to this action of carbon in a greater degree than the more powerful bases, thus leading to a partial separation.

As, however, animal charcoal contains calcium phosphate in large quantity, which must have a disturbing effect, the attempt was made to eliminate it by means of dilute hydrochloric acid; which was only partially successful, as on igniting the charcoal there always remained a considerable incombustible residue. A preliminary ex-

periment was, however, made with animal carbon approximately purified in this manner, and the earth separated by treatment with charcoal was subsequently most carefully purified. (See *Zeit. Anorganische Chemie*, iii., 48 and 49).

The solution of the earthy chloride used was freed from free hydrochloric acid as far as possible by evaporation; the clear solution was mixed with ammonia, until on heating there remained a small permanent precipitate, which was filtered off.

The bone-black, previously ignited, was put into the clear filtrate, containing in 200 c.c. 3 grms. of earth, using 10 grms. of carbon to 1 gm. of earth. After heating on the water-bath for two hours and allowing the liquid to cool, it was filtered, and the carbon was washed with distilled water until the filtrate no longer gave a precipitate with ammonia. The carbon was then incinerated, the earth dissolved out of the ash by warming with hydrochloric acid, the solution precipitated with oxalic acid, the oxalate ignited, and the earth then once more purified in the same manner as in the former determinations of the equivalents (iii., 48). The earth separated by the carbon

contained a $R = 155.94$; the portion not precipitated gave the atomic weight 138.7 .

To obtain unobjectionable results it was necessary to use a carbon containing no phosphoric acid, as the presence of the latter substance may have occasioned the above difference of the atomic weights. But the complete removal of phosphoric acid from earthy substances is well known not to be easy. Such a carbon was prepared by dissolving 150 grms. cane-sugar and 75 grms. potassium carbonate in water, evaporating down the solution, and heating the residue to 600° for eight hours, with exclusion of air. The mass obtained was pulverised, lixiviated with water, and finally washed upon a filter with dilute hydrochloric acid until every trace of potassium carbonate was removed. This carbon, used in the manner above

described, separated from a material, $R = 116.8$, a portion which, on determining its combining weight, was found to contain $R = 134.4$.

Hence it is demonstrated that a partial separation of the rare earths can be effected by means of porous carbon. But the quantities thrown down by the earth are rather trifling, *e.g.*, 0.05 gm. from 2 grms. earth on employing 8 grms. carbon. Hence it is not advantageous to work up a material of rare earths on this principle from the beginning.

The use of a porous carbon seems, however, very advantageous for separating from a rare earth small quantities of more feebly basic oxides, *e.g.*, yttria from an admixture of more feebly basic gadolinite earths, which readily cause it to take a slight yellowish colour. Thus from an yttria material, which, according to its analysis,

contained $\alpha R = 93.03$ ($Y = 90$) there was obtained by a single treatment with carbon an earth the equivalent of

which was found to be $R = 96$, a result which could not be obtained from this material in a single operation even by precipitation with aniline.

Porous carbon may therefore be used as a good separating agent in the final purification of the rare earths. It seems also advisable to examine the behaviour of an earthy salt with porous carbon if we wish to be satisfied of the unitary character of a rare earth supposed to be homogeneous.—*Zeit. Anorganische Chemie*, iii., p. 89.

On Aconitine.—A. Ehrenberg and C. Furfurst (*Four. Prakt. Chemie*).—The pure base melts at 193° to 194°, but very minute traces of a decomposition product depresses the melting point by 10°.

BEHAVIOUR OF SOME METALS WITH GASES.

By G. NEUMANN.

THE portion of this investigation relative to hydrogen has been executed by the author in conjunction with F. Streintz. Their attention was drawn to the question by the view that lead as the negative plate of a secondary element is capable of occluding hydrogen.

A proof for the correctness of this view could not be obtained by direct electrolytic experiments, as the arrangement of the experiment proved too difficult. Better results were obtained on allowing pure, dry hydrogen to pass through melted lead in a U-tube.

After the gas had been passed for a considerable time, the excess was driven out by nitrogen. Oxygen was then passed through, and this again was expelled by dry air. The water formed by the action of oxygen was received in calcium chloride tubes and weighed, and the quantity of hydrogen absorbed by the metal was thus calculated. In two experiments which could be regarded as successful the result was in one case 0.15 times the volume of the metal, and in the other 0.11 times. Hence the occluding power of lead for hydrogen seems demonstrated.

The next experiments were made with palladium. This metal, as is well known, occludes hydrogen very greedily. The experiments, as well as those with other metals still to be mentioned, were executed in an analogous manner to those on lead, *i.e.*, the dry hydrogen was passed over the heated metal. The metal was used as palladium black. Hydrogen was absorbed to the extent of 502.35 times the volume of the metal.

Platinum was examined as platinum sponge and platinum black. The latter acts more energetically, is raised to redness by absorption without the application of external heat, as is palladium by the absorption of oxygen. Platinum sponge occludes 49.30 times its volume of hydrogen. This figure varies considerably from that found by Graham. For an explanation of this difference we must refer to the original.

Gold occludes relatively much hydrogen; the action of oxygen upon the metal charged with hydrogen is not very strong. In two experiments there were obtained respectively, 46.32 and 37.31 times the volume of the metal. Here also the values were decidedly higher than those ascertained by Graham. The latter used gold from so-called assay-rolls, whilst the authors employed a preparation obtained by precipitating the chloride with oxalic acid.

Silver absorbs, according to the author's experiments, no hydrogen, whilst, according to Graham, silver wire occludes 0.211 times its volume. Aluminium absorbs 2.72 times its volume of hydrogen in thin sheets previously purified.

Iron in a state of fine division absorbs 19.17 times its volume. Copper occludes about four and a half times its volume.

Nickel, which in its chemical properties is intermediate between copper and iron, behaves similarly in its occlusive power for hydrogen. It occludes 17.57 volumes.

The absorption of hydrogen by cobalt is rather large, and the metal when charged with hydrogen becomes incandescent in a current of oxygen.

The occlusive power of some metals for hydrogen decreases on a repetition of the experiments. The authors explain this in the noble metals by an increase of density. This occurs according also to Graham. Copper and nickel on a repetition of the experiment show the same occlusive power. In the case of iron and cobalt, which behave like the noble metals, the authors have not yet found any explanation.

Neumann has examined the behaviour of the precious metals with oxygen by a method analogous to that above described.

The metals were ignited for some hours in pure oxygen, two calcium chloride tubes were then attached before the

occlusion tube, and a potash apparatus to observe the rapidity of the gas; the oxygen was displaced by air, and this, again, after cooling, by nitrogen. After the current has passed for half an hour, hydrogen was introduced and heat was applied. The water formed was received in the calcium chloride tubes, which were weighed after they had been successively traversed by nitrogen and air.

Silver on being thus treated absorbed 4.09 vols., which does not agree badly with Graham's result, according to which from 6.15 to 7.4 vols. were absorbed.

Gold absorbed 48.49 vols. of oxygen, whilst Graham observed no absorption. Neumann believes that this difference may be explained by the temperature of the experiment.

In case of platinum, concerning the absorptive power of which for oxygen there is much discrepancy among former observers, Neumann found occlusion of 77.14 vols. With palladium the author found a formation of suboxide, since the residue after treatment with oxygen contained 6.99 per cent, whilst Pd₂O contains 7.33 per cent.

Neumann considers that the absorptions of oxygen depend on a power of the metals to become oxidised at about 450°, the temperature of the experiment.—*Zeit. Anal. Chemie*, vol. xxxii., p. 72.

DETERMINATION OF CALCIUM TARTRATE.

By CH. ORDONNEAU.

WE take 20 grms. calcium tartrate, an average sample, pulverise them finely in the mortar, and add 20 c.c. of commercial hydrochloric acid at 20°, diluted in 100 grms. of water. The solution may be promoted by heating to ebullition. We make up 202–203 grms., according to the quantity of the insoluble matters, and filter. We take 50 grms. of the solution when cold, and pour it into a flask holding about 90 c.c. We add 2 c.c. of solution of citric acid at 25 per cent, and then 10 c.c. of solution of calcium acetate at 25 per cent (25 grms. calcium acetate and water to make up 100 c.c.). We agitate strongly, when crystals of calcium tartrate form after a few minutes. We then add 5 c.c. more of the same solution of calcium acetate, agitate, and allow it to settle for fifteen or thirty minutes. All the tartar is precipitated in a pure state.

We pour the whole upon a plain filter 9 c.m. in diameter, detach the tartar adhering to the flask with a slender piece of curved wood, wash the flask and the tartar from the filter with 30 c.c. of water in several portions.

The filter is then opened and laid on a plate of copper or sheet-iron above a water-bath. The paper dries enough to permit the separation of the tartar, which is transferred to a round nickel capsule 9 c.m. in diameter. The filter is dried completely, the tartar is detached and added to that in the capsule.

The capsule is then placed on the water-bath so as to dry the calcium tartrate completely. The desiccation is promoted by stirring the mass with a very pliable spatula. We cease when the tartar, which forms clots as long as it is moist, begins to flow like dry sand. At this moment we wipe the capsule and weigh the tartar obtained.

The result found, multiplied by twenty, gives the standard of the tartar if we have operated upon 5 grms. of substance. To this must be added 2 per cent to compensate for the loss on the filter and the solubility of calcium tartrate.

The exact moment of drying must be seized when the calcium tartrate contains 4H₂O. Each additional minute causes a loss of 0.10 per cent of tartar, but as the point is easy to seize (for it occurs suddenly on stirring the substance), there is no error in this respect beyond 0.20 per cent, which may be neglected.

By this process there are formed calcium tartrate, calcium chloride, and free acetic acid, which has no action on calcium tartrate. As the precipitation of the tartar is always effected in a very acid liquid, malic acid, if it is present, remains in solution and does not falsify the results.

The object of the citric acid is to dissolve the aluminium phosphate, which forms a lake with the colouring matter, and which the acetic acid does not dissolve. It is also without action upon calcium tartrate. It is preferable to precipitate in two portions, since the crystals of tartar are thus coarser, which renders it easier to seize the exact moment when the moisture is expelled.

If we wish to determine the total acidity of any tartar we must operate in the same manner, adding 25 c.c. of solution of calcium acetate in two portions. This quantity is sufficient for 5 grms. pure potassium bitartrate, and consequently the process is general.

The calcium tartrate must be washed, collected, and weighed. We have then to add 2 per cent to the amount found, and on multiplying the calcium tartrate by 0.576 we have the value in tartaric acid.

Second Process.—We take 50 grms. of the solution of tartar, which is poured into a porcelain capsule and heated to ebullition. We add then some drops of solution of phenolphthaleine, and then gradually, and with continual stirring, a clear milk of lime which has been strained through silk. The source of heat is extinguished or removed as soon as "bumping" sets in; the saturation is continued, giving the calcium tartrate time to subside after each addition of lime, and ceasing when neutrality is reached, which requires about five minutes. We add then to the liquid 2 c.c. of the citric solution at 25 per cent, stir, and allow it to subside. After some minutes the temperature is 50° to 60°, when we decant, pour the tartar upon a plain filter of 0.09 metre, and wash with 30 c.c. of water.

The calcium tartrate is dried as above, taking care not to break the filter. To the result obtained we add 4 per cent for the solubility of the substance in the liquid and the loss on the filter. Even if the quantity of malate exceeds 20 per cent, which is a very rare case, we need add only 3 per cent for accuracy, as the solubility is then lower. The quantity of malate is found by the deficiency of the result plus the insoluble matters to make up 100. On operating thus on pure calcium tartromalate, or on a mixture of the two salts in equivalent proportions, we find 99.50 per cent of calcium tartrate almost free from malate.

This process has the advantage of serving for industrial refining. In place of adding citric acid we leave a slight acidity, which dissolves the alumina and the phosphates. The tartar obtained is pure if the liquid is decanted whilst luke-warm, for complete refrigeration precipitates the calcium tartromalate to the extent of about 10 per cent of the tartar operated upon. This salt is collected and utilised in a fresh operation.—*Bull. Soc. Chim. Paris*, Series 3, ix.—x., p. 68.

THE GREENE-WAHL PROCESS FOR MANUFACTURING MANGANESE AND ALLOYS OF MANGANESE FREE FROM CARBON.*

By F. LYNWOOD GARRISON.

THE great objection to the use of ferro-manganese in the manufacture of steel has been its invariable association with considerable quantities of carbon, causing, when it is added to a low carbon steel to produce manganese-steel, a hardening of the steel, whatever may be the action of the manganese. There would seem to be commercial advantages in producing a ferro-manganese free

from carbon, so that the steel to which it was added would receive the beneficial effect of the manganese without the carbon contents being increased. Mr. Garrison believes the question of producing a ferro-manganese free from carbon to be solved by Messrs. Greene and Wahl.

The first attempt to produce metallic manganese in considerable quantities seems to have been made by Hugo Tamm in 1872. Native dioxide of manganese was heated with powdered charcoal or lampblack and oil in the presence of a powdered siliceous and fluor-spar flux. The manganese obtained having contained an appreciable amount of carbon, Tamm made attempts to remove this by fusing the metal under a layer of manganese carbonate. Tamm claimed to have made a metal having the composition—Manganese, 96.9; Fe, 1.05; carbon, 0.95; and other elements, 0.10; from a pyrolusite containing 50.5 per cent manganese and 3.5 per cent iron. The resultant metal, after refining this product under the fused coating of manganese carbonate, contained—Mn, 99.91; C, 0.025; Si, 0.015; Fe, 0.05. These results have not been confirmed, however, by later experimenters, and they are doubted. Messrs. Greene and Wahl's first experiments were made for the purpose of testing the correctness of Tamm's assertions, and were unsuccessful in decarbonising the metal to any extent. They then became convinced that the first step in such a process should be the removal of the iron combined with the manganese. After abandoning magnetic and electro-chemical methods, they found that nearly all the iron of rich manganese ore could be removed by digesting the pulverised ore with 30 per cent sulphuric acid, the manganese remaining practically unaffected. The percentage of iron can be reduced from 5 or 6 per cent to a few tenths in a few hours, and the waste acid can be utilised in making ferrous sulphate.

The reduction of the purified ore then became a puzzling problem; it was found impossible to produce manganese containing less than 6 per cent carbon by reduction with carbon, and this high percentage of carbon could not be removed in the later operations by fusion with an oxidising agent. Messrs. Greene and Wahl believe that a complete reduction of any manganese oxide by carbon yields, not a manganese, but a carbide having the definite form Mn_3C . For this reason manganese free from carbon cannot be reduced in the electrical furnace or in graphite crucibles. Experiments with the electrolysis of the fused baths of manganese chloride and manganese fluoride were futile, and it became evident that a reduction, in the entire absence of carbon, was necessary for the solution of the problem. Moreover, the compound to be reduced should be one of the oxides of manganese, as the use of halogen compounds on a commercial scale and the reduction by sodium were precluded by reason of the cost of their manufacture.

Messrs. Greene and Wahl, having determined that the reduction by means of metallic aluminum, which had been barely experimented with by Michel, Wöhler, Levy, and Langley, was the proper method, they soon found that neither clay nor graphite crucibles could be used in the operation—the graphite for reasons mentioned before, and the clay because of the energetic action of the aluminum upon the silica; experiments yielding a siliceous manganese containing in some instances as high as 12 per cent silicon. Calcined magnesite, however, was found to answer the purpose, and a graphite crucible lined with this afforded excellent results. In producing this pure manganese, the manganese dioxide is reduced to monoxide by heating in a stream of reducing gas. It is then mixed with granulated aluminum and with a flux of lime and fluor-spar. The mixture is then placed in the magnesite-lined black-lead crucible, and placed in a furnace commonly employed in melting brass. When the contents have reached a bright red, the aluminum begins its energetic reducing action upon the manganese monoxide, and in a few minutes the reaction is complete. The heat liberated liquefies the contents of the crucible,

* A Paper read before the American Institute of Mining Engineers, Montreal Meeting.

and brings them to a white heat. The inventors state that they have obtained a yield as high as 2·84 parts of manganese per unit of aluminum, equal to 94·5 per cent of the theoretical yield. The following is the reaction that occurs:— $\text{Al}_2 + \text{MnO} = \text{Al}_2\text{O}_3 + 3\text{Mn}$. The metal obtained is dense and homogeneous, with a steel-grey colour and a pinkish to reddish bronze tint. It is hard and brittle, having an irregular fracture. The specific gravity varies between 7·26 and 7·38, or 7·32 on an average. Its average composition is Mn, 96·5; Fe, 2; Si, 1·5. It retains but the slightest trace of aluminum.

In operating a small plant capable of producing about 2 tons of manganese per week, the inventors state that 1560 lbs. of aluminum and 5 tons of manganese ore will be required. Basing their calculations of the present market value of aluminum at 55 c. per pound, and manganese ore at 40 dollars per ton, they find that the manganese will cost about 7·60 dollars per long ton, or about 34 cents per pound.

As yet the process has been conducted on a laboratory scale only, but it would seem to have many possibilities. —*Engineering and Mining Journal*.

GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 105).

Erdmann and Marchand's Work.

THERE is no need of our here repeating what was said in the prefatory note (*ante*). We therefore pass at once to an account of our experiments on the dehydrating powers of chloride of calcium and caustic potash. Our apparatus consisted of the following successive communicating parts:—

- I.—A Pisani gasholder, containing a little over 12 litres of air, shut up over dilute solution of caustic potash or soda, followed by—
- A.—A large tower charged with fragments of recently fused caustic potash.
- B.—A tared U-tube, charged with the same reagent.
- C and D.—Two U-tubes, charged with vitrioled pumice; both tared.
- E.—A wash bottle, containing water.
- F and G.—Two U-tubes charged with fragments of recently fused chloride of calcium; both tared.
- H.—A U-tube, charged with vitrioled pumice; tared.
- K.—A similar tube, untared.

The U-tubes intended for the determination of the weights of absorbed matter were all tared, not with weights, but with similar tubes of as nearly as possible the same displacement. Each tare-tube contained a quantity of selenite adjusted so that it displaced very nearly the same volume of air as the chloride of calcium or caustic potash in the working tube. Our U-tubes were all of that now popular kind in which the gas enters and goes out through laterally soldered-in short tubes, and the orifices are provided with perforated ground-in hollow glass stoppers, so that one can close either or both sides by a turn of the stopper, or open them to admit the respective current of gas.†

The necessary tarings having been effected, and the apparatus put together, the air from the Pisani was turned on and made to pass through the apparatus at a suitable rate, until a sufficient volume had accumulated in the graduated Pisani bottle. The following diagram will facilitate the reading of the tables of results:—

Pisani KHO KHO H_2SO_4 H_2SO_4 Water CaCl_2 CaCl_2 H_2SO_4 H_2SO_4
I. A B C D E F G H K

* *Proceedings of the Philosophical Society of Glasgow.*

† Both remarks apply to the vast majority of the respective experiments reported on in the preceding section.

First Set.

Experiment—

	I.	II.	III.	
Temperature ..	12—14°	12·7—14°	14—16°	
Volume of air, ..	12	2·5	11	litres.
which passed in	4	1·25	2	hours.
KHO, B, gained ..	0·6	0·15	—0·2	m.grm.
Vitriol, C, gained .	1·35	0·15	0·1	„

After Water.

CaCl_2 , F, gained..	—	—	70·4	m.grms.
CaCl_2 , G, gained..	0·2	nil	12·8	„
Vitriol, H, gained .	2·2	0·45	2·5	„

From these numbers we see that the caustic potash tower dehydrated the air so completely that the potash U-tube following it had little or nothing to do; and, assuming oil of vitriol to be a perfect dehydrator for gases, that in experiments II. and III. at least, the caustic potash dehydrated the air as good as completely. The fused chloride of calcium dehydrated the moist air coming from E so completely, that only 0·183, 0·180, 0·227 m.grm. of water were left in every litre of air. In a corresponding experiment by Fresenius the residuum of water amounted to 0·97 m.grm. per litre. (See p. 179 of his memoir.) Fresenius says that his chloride of calcium was fused and put into the tubes while still hot. This is exactly what we did, except that we allowed our preparation to cool before filling the tubes with it; hence we are at a loss to explain why our tubes worked so much better than his. But we had no doubt in our mind that Fresenius's chloride of calcium was a fair preparation, and took it to be a fair presumption that Erdmann and Marchand's preparation was no better than that of Fresenius. We therefore spoiled our chloride of calcium expressly by passing moist air through it until it had gained 130 m.grms. in weight, and then resumed our experiments. In experiments IV., V., VI., the wash-bottle E and the two chloride of calcium tubes were immersed in a water-bath kept at 25°. In experiments VII. and VIII. only the wash-bottle and the first chloride of calcium tube were kept at 25°, the second CaCl_2 tube was not artificially heated or cooled.

Second Set.

Experiments.

	IV.	V.	VI.	VII.	VIII.
Temp. of air..	13·5-16·5	13-16	11·5-15°	11-15°	—
Temperature of water kept at 25° throughout the series.					
Volume of air ..	10	10	10	10	10 litres.
Time	2	2·25	2·25	2·25	2 hours.
Gain of B.. ..	0·6	0·5	0·3	0·5	* m.grm.
Gain of C.. ..	0·5	—0·1	0·3	0·3	* m.grm.

After Water.

Gain of F.. ..	122·8	129·6	114·8	125·0	* m.grm.
Gain of G.. ..	14·0	9·3	2·9	6·6	2·0 „
Gain of H.. ..	6·3	5·0	7·8	6·0	5·0 „

Hence, 1 litre of chloride of calcium dry air contains—

Of water 0·63 0·5 0·78 0·60 0·5 m.grm

While 1 litre of KHO dry air contains—

Of water 0·05 0·0 0·03 0·03 * m.grm.

* Not determined on account of want of time.

We deem it worth while to state that, even after the eighth experiment, the chloride of calcium in the outlet limb of tube G was still glassy in appearance, and that even that in the inlet end was not visibly spoiled. What we mean to say is that it would have passed in any laboratory for fair enough chloride of calcium for ordinary work. From our experiments and Fresenius's conjointly, we derive the conviction that a gas which has been dried by means of apparently well-conditioned chloride of

calcium may contain as much as 1 m.grm. of water per litre. Fused caustic potash, on the other hand, dries a gas quite completely. We assert this the more confidently, as our second series of syntheses (which came long after the experiments now under discussion) proved to us again and again, that a gas which has passed over a long enough column of recently fused caustic potash gives up no water even to phosphoric anhydride.

On these facts we base the following hypothesis concerning Erdmann and Marchand's work:—In their last four experiments (and only these need to be taken into account), the hydrogen which entered their reduction-tube was free of any kind of oxygen, because they avoided the use of oil of vitriol as a dehydrating agent, and passed their gas over red-hot metallic copper before it reached the final dehydrator. But the surplus hydrogen which passed through the reduction-tube at the end of the experiment, and the air which followed it, carried away with them an appreciable weight of vapour of water, because there was only a chloride of calcium tube at the outlet of the water receptacle to catch it. Assuming, now, that they used (let us say) 3 litres of surplus hydrogen and 3 litres of air, for every 8 grms. of oxygen used as oxide of copper, and that their chloride of calcium was at a par with Fresenius's as a dehydrator, about 6 m.grms. of the water which they produced failed to find its way to the balance. Now, their reported water-weight was almost exactly = 9.000 grms. per 8 grms. of oxygen; hence their total water actually produced was equal to 9.006 grms.; and hence their real value for H (if O=16), is 1.006, and not 1.000.

Dumas produced too much water, but may have underdetermined its weight by forgetting the vacuum reduction. Erdmann and Marchand produced the correct amount of water and weighed what they had on the balance correctly, but they lost some of their water before it came to the balance.

We will now pass to our own first series of syntheses which, as may be remembered, was made before we had discovered the reducing action of vitriolised pumice on hydrogen gas.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 16th, 1893.

Prof. A. CRUM BROWN, F.R.S., in the Chair.

It was announced that the following changes in the Council were proposed by the Council:—

As President: Professor H. E. Armstrong, *vice* Professor Crum Brown.

As Vice-Presidents: Dr. E. Atkinson and Mr. C. O'Sullivan, *vice* Professor Hartley and Mr. Warrington.

As Secretary: Professor Dunstan, *vice* Professor Armstrong.

As ordinary members of the Council: Messrs. C. F. Cross, Bernard Dyer, D.Sc., Lazarus Fletcher, M.A., and W. A. Shenstone, *vice* Mr. H. Bassett, Professor Ferguson, Mr. J. Heron, and Mr. S. U. Pickering.

Messrs. Holland Crompton, T. S. Dymond, and Dr. T. A. Lawson were appointed to audit the Society's accounts.

Ordinary certificates were read for the first time in favour of Messrs. Lawrence Augustus Baine, Dipton, Lintz Green, Newcastle-on-Tyne; George Clayton, School of Pharmacy, 100, Burlington Street, Manchester; Robert George Grimwood, 41, Lady Margaret Road, St. John's College Park, N.W.; Alfred Rowland Gower, 39, Stafford Street, Barrow-in-Furness; Hooper Albert Dickinson Jowett, 3, Fern Bank, Lancaster; Herbert

Lloyd, Philadelphia, U.S.A.; Edmund George Lamb, 29, Great Cumberland Place, W.; James Mason, Cambois, Blyth, Northumberland; Henry John Monson, 15, Palace Street, Buckingham Gate, London, S.W.; William Henry Oates, Broomhall Park, Sheffield; S. Parrish, 15, Fenton Street, Woodhouse Lane, Leeds; Frank P. Vandenbeigh, B.S., M.D., Buffalo, New York; A. F. Watson, 11, York Place, Edinburgh.

The following were duly elected Fellows of the Society:—John Pedrozo D'Albuquerque; William Thomas Boone; John Edwin Brockbank; Edward Brooke; George Davey; Daniel O. Sydney Davies; Charles Dreyfus, Ph.D.; Samuel Felix Dufton, B.A., D.Sc.; Francis P. Dunnington; Alexander Stanley Elmore; Frederick George Fuller; Albin Haller; George Nevill Huntly; Arthur John Heath; Wesley Lambert; Charles M. Luxmore; Fred. Marsden; Herbert Bloome Mole; William J. Martin, jun., M.D.; Robert Henry Owen; Charles Platt, A.C.; James Robert Thackrah, M.A., Ph.D.; Charles Thomas Tyrer; John William Towers; John Charles Umney; Henry C. White; Willoughby Walke; Charles E. Waite; William Ernest Wheeler.

Of the following papers those marked * were read:—

*113. "Note on the Preparation of Platinous Chloride, and on the Interaction of Chlorine and Mercury." By W. A. SHENSTONE and C. R. BECK.

In a paper read before the Society last year (*C. S. Trans.*, 1892, 445) we gave the results of the analysis of the gas evolved on igniting various specimens of platinous chloride *in vacuo*, showing that in every case very sensible quantities of hydrogen chloride and oxygen were present. The greatest amount of impurity was found in a specimen derived from the salt prepared by heating hydrogen platinichloride *in vacuo* in a tube containing solid potash, as recommended by Pigeon (*Compt. Rend.*, 1892). This last fact and Pullinger's description of his method of preparing anhydrous platinic chloride (*C. S. Trans.*, 1892, 422) led us to conclude that probably a more satisfactory product, at any rate as a source of chlorine, would be obtained by heating hydrogen platinichloride at a high temperature in a current of dry hydrogen chloride.

Experiment I.—Some hydrogen platinichloride was heated at the boiling-point of mercury in a current of dry hydrogen chloride during fifteen hours, and the hydrogen chloride was then displaced by dry air. A part of the product was ignited *in vacuo*, and the gas which was given off was examined in the manner previously described (*loc. cit.*). We found that the residue from the action of mercury only amounted to 0.156 per cent. This residue was partly soluble in water as before. The gas made in this way therefore contained 99.84 per cent of chlorine.

Experiment II.—A portion of the product of the first experiment was heated in a current of dry hydrogen chloride at about 500° during many hours by placing it in a glass tube surrounded by a well-fitting glass jacket immersed in a bath of molten nitre; at the end of the operation the hydrogen chloride was expelled by means of dry air. The process was rather difficult to carry out, as the complete decomposition of the salt easily takes place if the temperature too much exceeds the melting-point of silver chloride, some decomposition occurring even at that temperature.

A portion of the product of this experiment was placed in a glass tube, which was then exhausted as in our previous experiments; it contained no drying material, but both the tube and its contents were heated to drive off moisture. Chlorine was generated from the chloride by igniting it *in vacuo*, and the residual platinum having been removed, one end of the tube was broken under mercury. Although we had intentionally neglected to dry the gas, we were at once struck with the fact that the action between this sample of chlorine and mercury was decidedly less active than in the case of any of the specimens previously examined, and when the action of

mercury was at an end so little residue was left that its analysis by the method formerly described seemed useless. The part of the narrow tube which had contained the residual gas was therefore cut off and calibrated: it was thus found that the residue amounted to only 0.06 per cent of the gas taken. The residue was partly soluble in water.

We have not determined the total chlorine in the platinous chlorine made in this way, as we do not think it consisted of pure platinous chloride; it probably contained a little platinum, but as a source of chlorine it seems to be very superior to the product of the more familiar processes.

We have previously suggested that the marked activity of even the most carefully dried chlorine towards mercury is probably due to the presence of impurities in the gas. The sluggish action of chlorine and mercury observed in our second experiment, in which the chlorine employed, though not quite dry, contained much less hydrogen chloride and oxygen than any that we have previously examined, is therefore interesting and suggestive.

Shortly after the publication of our former paper on this subject, Professor Victor Meyer called our attention to the fact that in his later experiments on the density of chlorine he assured himself that the other gases present in the chlorine employed were insufficient in quantity to materially affect the chief conclusion he drew from his results (*Ber.*, xiii., 1721). We are anxious to mention this, although we made no direct reference to the subject in our paper, as one of our remarks might very possibly be supposed to imply the contrary.

DISCUSSION.

Mr. GROVES having asked whether the authors had made any further experiments in the direction of fractionally evaporating liquid chlorine, Mr. SHENSTONE, in reply, stated that by fractionating the liquid they had obtained chlorine which, when tested by mercury, was found to be almost as nearly pure as that obtained from platinous chloride. This chlorine, however, acted rapidly on mercury, even after it had been highly heated, and he was inclined to suspect the presence of traces of oxy-compounds in it. It was worth while mentioning that recently roasted chlorine does not appear to cause the adhesion of mercury to glass in anything like the same degree that ozone or unroasted chlorine does. Whether this is due to a change in the gas or to a change on the surface of the glass he could not say.

*114. "The Action of Phosphoric Anhydride on Fatty Acids." Part III. By F. STANLEY KIPPING, Ph.D., D.Sc.

Results of an investigation of the behaviour of some of the fatty acids with phosphoric anhydride have been communicated to the Society in previous papers (*Trans.*, 1890, 532, 980); it is now shown that caprylone, $(C_7H_{15})_2CO$, nonylone, $(C_8H_{17})_2CO$, and myristone, $(C_{13}H_{27})_2CO$, can be easily prepared from the corresponding fatty acids and phosphoric anhydride.

The hydroximes of these ketones, the secondary alcohols obtained from the ketones by reduction, and the acetyl derivatives of some of the alcohols have been prepared and characterised, and are described in the papers. It is also shown that mixed ketones of the general formula $R \cdot CO \cdot R'$ are produced when a mixture of two fatty acids is treated with phosphoric anhydride at a moderately high temperature; the mixed ketone is accompanied by two simple ketones, just as is the case when a mixture of the barium salts of two fatty acids is submitted to dry distillation.

The question of the existence of isomeric modifications of the hydroximes of fatty asymmetrical ketones is briefly referred to.

It would appear from the results described in this paper and from those already recorded, that treatment with phosphoric anhydride is one of the simplest and most rapid methods by which a fatty ketone of the general

formula $(C_nH_{2n+1})_2CO$ can be prepared from a fatty acid $(C_nH_{2n}O_2)$, the product being easily isolated and the yield fairly good, especially in the case of the higher acids.

*115. "Regularities in the Melting points of Certain Paraffinoid Compounds of Similar Constitution." By F. S. KIPPING, Ph.D., D.Sc.

Having obtained considerable quantities of many of the fatty ketones $(C_nH_{2n+1})_2CO$, the author was able to prepare and characterise their more important derivatives; e.g., various members of the series of hydroximes $R_2C:NOH$, secondary alcohols $R_2CH \cdot OH$, and ethereal salts $R_2CH \cdot OAc$.

Attention is drawn to certain regularities observed on contrasting the melting-points of these compounds; it is also pointed out that the melting-points of all ketones of the general formula $C_nH_{2n}O$ cannot be calculated by means of the formula suggested by Mills (*Phil. Mag.*, 1884), inasmuch as isomeric ketones frequently melt at different temperatures.

DISCUSSION.

Mr. A. R. LING drew attention to the similarity in the melting-points of many chlorinated derivatives of *p*-benzoquinone and of the corresponding quinols and their diacetyl derivatives as compared with those of the analogous bromo- and chlorobromo compounds. The agreement seems to be wanting in the para-dihalogen derivatives, but in all other cases it is sufficiently close to be remarkable. The displacement of chlorine by bromine is usually attended by a rise in the melting point, but meta-chlorobromoquinone and its derivatives melt at slightly lower temperatures than the corresponding dichloro-compounds. Only two iodoquinones are known, but their melting-points do not exhibit the least similitude as compared with those of their analogues.

*116. "Some Relations between Constitution and Physical Constants in the case of Benzenoid Amines." By W. R. HODGKINSON and LEONHARD LIMPACH.

A study of the formyl and acetyl derivatives of certain homologues of aniline shows, amongst other things, (a) that the entry of alkyl groups into the nucleus affects the melting- and boiling-points in a regular manner; (b) that the conversion of formyl into acetyl also involves an alteration in physical properties in extent the same as that produced by introducing CH_3 into the nucleus in an *ortho*- or *para*-position relatively to the amido-group; and (c) that the same (or any?) alkyl group entering the nucleus in the meta-positions has no effect on melting- or boiling-point. Several numerical regularities are also apparent.

Thus, taking the melting-points of the methylamido-benzenes as first examples:—

Formanilid	46'	Acetanilid	114°
Formylxylyl	76	Acetylxylyl	144
	—		—
Difference	30	Difference	30

That the introduction of methyl into the meta-position has no influence on the melting-point is shown by the fact that the following substances melt at the same temperature within a degree:—

Acetmesidid	NHAc:Me:Me:Me=	
	=1:2:4:6.	M.p. 216°.
Acettetramethylamido- benzene	{ NHAc:Me:Me:Me:Me=	
	{ =1:2:3:4:6.	M.p. 215°.
Acetpentamethylamido- benzene	{ NHAc:Me:Me:Me:Me:Me	
	{ =1:2:3:4:6:6.	M.p. 214
		to 215°.

That the CH_3 of the acetyl has an effect on the *ortho*- and *para*-position in the nucleus seems evident, as 1:2:4-formylxylyl has the same melting-point as acetanilid (114°). Similarly, 1:3:5-acetylxylyl and 1:2:3:4:5-tetramethylformanilid have the same melting-point, viz., 144°.

The tetramethylformanilid can be imagined as built up of 1:3:5-formylxylylid and 1:2:4-formylxylylid.

Melting-point of 1:2:4-formylxylylid	113.5°
" 1:3:5 "	76.5
		190.0
" formanilid	46.0
" 1:2:4:5-tetramethylformanilid		144.0

Formylmesidid and acetylxylylid, $\text{NHAc:Me:Me} = 1:2:6$, have the same melting-point (176°). In this case the influence can only be exerted on one position (the para-), as both the ortho-positions are occupied.

Similarly, formylmesidid and 1:2:3-acetmetaxylylid both melt at about 176° , and acetmesidid and 1:2:3-propionylxylylid at about 216° .

As an example of numerical relations, taking formyl compounds, formanilid melts at 46° , pentamethylamido-benzene at 217° : now the melting-point of formanilid (46°) plus $2(34) = 114^\circ$, which is the melting-point of formylmetaxylylid, $\text{NHF:Me:Me} = 1:2:4$; again, the melting-point of formanilid plus $4(34) = 182^\circ$, which is the melting-point of $\text{NHF:Me:Me:Me:Me} = 1:2:3:4:6$.

The formyl compounds of aniline, *p*-toluidine, 1:2:4-metaxylylidine, and mesidine form a series:—

Aniline (46°); <i>p</i> -toluidine (52°); 1:2:4-xylylidine (114°);	
46	$= 46 + 6 \quad 46 + 6 + 62$
mesidine (176°), &c.	
	$= 46 + 6 + 2(62)$.

Similarly in the case of the corresponding acetyl compounds:—

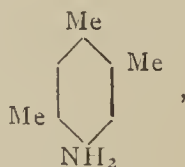
Aniline (114°); <i>p</i> -toluidine (147°); 1:3:4-xylylidine (181°);	
$= 46 + 2(34) \quad = 46 + 3(34) \quad 46 + 4(34)$	
mesidine (216°).	
	$46 + 5(34)$.

The different positions are not in all cases of equal value. Thus, pentamethylformanilid melts at 217° , and $46 + 5(34) = 216^\circ$, which might indicate equality of the methyl groups, or rather of the positions in benzene. But when CH_2 is introduced into 1:2:4-xylylidine to form mesidine, the melting-point rises 62° , so that the formula becomes—

$$\begin{array}{r} 2 \times 34 = 62^\circ \\ 1 \times 62 = 62 \\ 1 \times 46 = 46 \\ \hline 176 \end{array}$$

On introducing methyl into the meta-position, the melting-point rises to 182° in the case of 1-amido-2:3:4:6-tetramethylbenzene. The CH_3 groups appear again equivalent.

Again, taking away a methyl in the ortho-position leaves a pseudocumidine,—



melting at 121° , a drop of 62° .

These examples will suffice at present to show that definite relations between melting-points apparently do exist in the case of methylamidobenzenes. The authors have examined a number, and are gradually preparing other alkylamidobenzenes, containing ethyl, butyl, &c., and find also great regularities from which they hope to be able to state a general law. Many of the published data relating to melting-points undoubtedly require careful revision.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, February 24th, 1893.

Prof. A. W. RÜCKER, F.R.S., President, in the Chair.

MR. EVERETT, jun., read a paper "On a New and Handy Focometer," by Prof. J. D. Everett, F.R.S., and exhibited the instrument described.

The focometer is constructed on the principle of the "Lazy tongs," and so arranged that the distance between the object and screen can be varied, whilst the lens is automatically kept midway between the two. This gives sharpest definition and the simplest calculation. The lazy tongs has eight cells formed by eighteen bars $13'' \times \frac{3}{4}'' \times \frac{1}{4}''$, and is capable of being extended to about eight feet or closed up to about one foot. Brass pins about $\frac{1}{4}$ inch diameter and $1\frac{1}{2}$ inches long project upward from each joint in the middle row, and serve as supports for clips carrying the lens, object, and screen. The instrument can be used for any lens whose focal length lies between 24 inches and 1 inch or less. To avoid error due to play in the joints, it is desirable to open or close the frame from both ends. The two chief disadvantages of the focometer are, first, its liability to flexure when much extended, and second, the rotation of the pins carrying the lens, &c., which necessitates re-setting of the clips after a large alteration of length has been made. Details respecting the most appropriate objects and screens, and practical hints about the working of the instrument are given in the paper. The question of what accuracy is obtainable is also briefly discussed.

Mr. A. HILGER thought the instrument was too flexible to be used for accurate work.

Mr. BLAKESLEY said it would be a great improvement if the pins could be prevented from rotating. For this purpose it might be advantageous to slot the heads of the pins so as to fit on a straight bar. He also suggested that by using a plane mirror close behind the lens the light would be reflected back and the length of the focometer could be reduced by one half.

The PRESIDENT thought Prof. Everett never intended the instrument to compete, as regards accuracy, with the elaborate and expensive apparatus now used; but nevertheless, the focometer was a very valuable one, especially for students' work, and was particularly well adapted to impress upon them the facts relating to conjugate foci.

A paper on "A Hydrodynamical Proof of the Equations of Motion of a Perforated Solid, with Applications to the Motion of a Fine Framework in Circulating Liquids," by G. H. BRYAN, M.A., was read by Dr. C. V. BURTON.

The object of the paper, which is a mathematical one, is to show how the equations may be deduced directly from the pressure equation of hydrodynamics, without having recourse to the laborious method of "ignoration" of co-ordinates. The general hydrodynamical equations of a perforated solid are first considered, and the pressure equation expressed in terms of the velocity, potential, density, and the translational and rotational velocities of the liquid. The expressions for the mutual reaction between the solid and liquid are then reduced to the required form by repeated applications of Green's formula, and the results made use of for writing down the equations of motion of the solid. The author then shows that the motion of the solid can be determined in terms of Routh's modified Lagrangian function, and the form of that function found. The results are applied to determine the motion of a light framework of wires. When the framework has a single aperture it is shown that no force produces motion in its own direction, and no couple produces rotation about its own axis. In the case of a fine, massless, circular ring, the direction of whose axis is taken as the axis of x , a constant force along the axis of y produces uniform rotation about the axis of z , and a constant couple about the axis of y produces uniform translation along the axis of z . In conclusion, the author states

that the results might be made to furnish mechanical explanations of certain physical phenomena.

Appended to the paper is a note by Dr. Burton relating to the proper measurement of the impulse of cyclic motion, and in a further note Mr. Bryan shows how the equations of motion may be deduced from Dr. Burton's suggestions.

The PRESIDENT said the author had done good service by attacking the difficult problem by elementary methods. He had also arrived at some very interesting conclusions, particularly the one showing that a perforated body moving through a liquid required no force to keep up the motion.

Dr. C. V. BURTON made a communication "*On Plane and Spherical Sound-waves of Finite Amplitude.*"

The first part of the paper refers to plane-waves. This subject had been considered by Riemann, but Lord Rayleigh had criticised that part of Riemann's work where it is held that a state of motion is possible, in which the fluid is divided into two parts by a surface of discontinuity propagating itself with constant velocity, all the fluid on one side of the surface of discontinuity being in one uniform condition as to density and velocity, and on the other side a second uniform condition in the same respects. After quoting Lord Rayleigh's criticism, the author shows that the same objection applies when the velocity and density on either side of the surface may vary continuously in the direction of propagation, and the velocity of propagation of the surface of discontinuity is also allowed to vary. In each case the assumed motion violates the condition of energy, and can only exist under that special law of pressure for which progressive waves are of accurately permanent type. Enquiry is then made as to what becomes of waves of finite amplitude after discontinuity sets in (which condition must always occur with plane-waves), in the course of which it is pointed out that the front of an air disturbance, produced by a moving source which starts impulsively, travels faster than the source, even if the velocity of the source exceeds that of feeble sounds. A mechanical analogy is given which suggests that a dissipative production of heat takes place when discontinuity occurs.

In all cases Riemann had assumed that pressure is a function of density only, according to the isothermal or adiabatic law, and thus failed to take account of any heat which may be dissipatively produced.

The first part of Burton's paper is concluded by a short reference to Dr. Tumlirz's work on the subject, who infers that as soon as a discontinuity is formed it immediately disappears again, this effect being accompanied by a lengthening of the wave and a more rapid advance of the disturbance. In this way Dr. Tumlirz seeks to explain the increased velocity of very intense sounds. The author, however, considers that an increased velocity can only ensue when the motion has become discontinuous.

Part II. of the paper deals with spherical waves, and contains a mathematical investigation into the conditions under which the motion remains continuous or becomes discontinuous. The criterion is found in the finitude or infinitude of a certain integral. It is shown that if viscosity be neglected, then under any practically possible law of pressure the motion in spherical sound-waves always becomes discontinuous. For waves diverging in four dimensions some cases occur in which the motion remains continuous. The general question of spherical sound-waves of finite amplitude is then treated of, and the paper concludes with a method of finding the differential equation of an infinitesimal spherical disturbance which is superposed on a purely radial steady motion.

Prof. A. S. HERSCHEL enquired whether the nature of the solution for plane-waves of finite amplitude was similar to that for ordinary wave-motion? In the latter case everything depended on the instantaneous impulses, for these alone determined the nature of the wave.

Referring to Mr. Bryan's paper, he (Prof. Herschel) asked if the author could apply his equations to centrifugal fans. A particular kind of double fan had recently been tested, and gave very anomalous results which had not yet been explained.

The PRESIDENT said Mr. Boys' experiments on flying-bullets might have some bearing on Dr. Burton's paper. If the conclusions there stated were correct, then the velocity of the air in front of a bullet should be greater than that of the bullet, even if the latter was travelling faster than ordinary sound-waves. He now asked Mr. Boys if his photographs gave any evidence of this.

Mr. Boys said the fact that the photographs showed disturbances in front of the bullet proved that the disturbance travelled faster. In one case, where a large bullet was moving at a velocity rather greater than that of ordinary sound in the medium, the front of the disturbance was about half an inch in advance of the bullet. In another instance, where the bullet was smaller and the velocity greater, the distance which the disturbance was in advance of the bullet was somewhat less. In all cases, even when the velocity of the bullet was four times that of sound, the character of the effects remained the same.

Dr. BURTON replied to the points raised.

INSTITUTE OF CHEMISTRY.

THE Annual General Meeting of the Institute of Chemistry of Great Britain and Ireland was held on March 1st at 30, Bloomsbury Square, W.C., the premises recently acquired by the Institute.

The Report of Council and Balance Sheet for 1892 having been presented and approved, the Council and Officers for the ensuing year were elected, and the President, Dr. William A. Tilden, F.R.S., delivered an address in which, after referring to the satisfactory progress which had been made by the Institute during the past year, he proceeded to explain the new curriculum recently adopted by the Council for the training and examination of Associates, and the proposals which had been brought forward by the Censors with the object of regulating the professional conduct of Members of the Institute.

The numbers on the Register now are 826 members and 109 students, as compared with 823 members and 34 students at the date of the last Annual General Meeting.

NOTICES OF BOOKS.

Rules for the Spelling and Pronunciation of Chemical Terms. Adopted by the American Association for the Advancement of Science in 1891.

THESE proposals, issued by the Bureau of Education, Washington, bear the signatures of Professors T. H. Norton, E. Hart, H. Carrington Bolton, and James Louis Howe, and recommend themselves to all English-speaking communities. In some cases, however, we venture to suggest that the proposed reforms might, without any risk of confusion, have been carried a little further.

The following general rules are laid down:—

1. The pronunciation is as much as possible in accord with the analogy of the English language.
2. Derivatives retain, as far as possible, the accent and pronunciation of the root-word.
3. Distinctly chemical compound words retain the accent and pronunciation of each portion.
4. Similarly sounding endings for dissimilar compounds are avoided.

A few alterations are made in the orthography of the names of the elements. Thus, for sulphur it is proposed to write sulfur, for which there is every reason, since the word is not of Greek origin. The names of the halogens

are to drop the final *e*, and have the *i* in the last syllable pronounced short. Here we think a little further change would be desirable; we would suggest to cancel the last syllable of the names of the halogens altogether, and write simple chlore, fluor, &c. Then we would drop the needless *us* of phosphorus, and write phosphor. Manganese we would convert into *mangan*, which would make the word less liable to be confounded with magnesium.

The recommendation is given to abrogate arsenetted (or arseniuretted) hydrogen and the analogous antimony, sulfur, &c., compounds in favour of arsin, stibin, phosphin. Benzene and toluene are to be used in place of benzol and toluol. This change, however, has been in part anticipated. Not a few chemists, whilst adopting benzene and toluene for the pure chemical individuals, retain benzol and toluol for the crude commercial products.

We have always used the terms "strength" or "standard" in place of titre, or, as it is written in America, "titer." We also use, as it is here recommended, "gramme," since "gram" is very apt to be confounded with grain. The termination "meter" is generally used in the names of pieces of apparatus, but in the names of measures we always write "metre." We are glad to see that the authors do not seek to spell barium as it is generally done on the Continent. The names glycerol, resorcinol, mannitol will not be very readily adopted in place of glycerin, resorcin, and mannite; nor are the pronunciations oxid, hydrid, &c., likely to find early favour. Perhaps the disagreeable custom of pronouncing oxygen and its paronyms as if written "ogsygen" does not prevail in America.

We wish some of our writers of elementary treatises on chemistry would take a leaf or two out of the book of the American chemists.

On the Preservation of Solutions of Hydrogen Sulphide. ("Sur la Conservation des Dissolutions de l'Acide Sulhydrique.") By Professors A. E. SALAZAR and Q. NEWMAN, of the Naval Military School of Chili. Translated from the Spanish by MANUEL A. DELANO. Member of the Scientific Society of Chili and of the Chemical Society of Paris. Paris: Imprimerie de la Cour d'Appel, 1892.

THE authors draw from their experiments the following conclusions, which will now scarcely be called in question:—

The solution of H_2S when made in pure water or in Lepage's mixture (water and glycerin) preserves the strength the less it is exposed to the action of air. For the preservation of the solution it is highly advantageous to dissolve the H_2S in Lepage's mixture and not in water, as in the former the oxidation of the gas is slower than in pure water.

Light has little influence on the speed of oxidation, whether the H_2S is dissolved in water or in the Lepage mixture. The oxidation is, however, more rapid in light than in darkness. Certain organic substances, added in small proportions to watery solutions of H_2S modify the progress of oxidation, either by acceleration or retardation.

Helbing's Pharmaceutical Record. No. X., October, 1892. Reprinted January 25, 1893. London: 63, Queen Victoria Street, E.C.

Notes on Eucalyptus Globulus and its Uses. By HARRY BENJAMIN, M.B. (Hobart). London, 1892.

THESE two pamphlets are written with a view to enlighten the public on the sanitary and medicinal properties of the true eucalyptus oil, obtained from the "Blue Gum Tree" of Tasmania, and to point out the difference of its composition and effects from those of preparations often substituted for it. Some of these oils are obtained from the "Peppermint Gum Tree" (*Eucalyptus amygdalina*), and others from the Mallee Scrub (*Eucalyptus dumosa*). The

two latter are certainly derived from members of the great Eucalyptus tribe, but they are poor in eucalyptol and too irritating for use either internally or externally.

Where the *E. globulus* or true "fever tree" grows, fevers are very rare and low forms of animal and vegetable life dislike the locality.

Fruit trees experimentally mulched in autumn with leaves of *E. globulus* are found next season free from blights and fungi. If a little of this oil is injected into a rose tree covered with aphides, the vermin all disappear in a few days. It is therefore exceedingly unfortunate that the products of *E. amygdalina* and *E. Dumosa*, relatively poor in eucalyptol, are commonly sold under the general, though misleading name of eucalyptus oil.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 8, February 20, 1893.

At the meeting of the Academy for nominating a correspondent for the section of chemistry, vice the late Prof. Stas, Prof. Kekulé was elected. He obtained forty-seven votes as against two given to Prof. Mendeleeff, and one each given to Prof. Cannizzaro and Sir H. Roscoe.

Preparation of Uranium at a High Temperature.—Henri Moissan.—This paper will be inserted in full.

Rapid Preparation of Chrome and Manganese at High Temperatures.—Henri Moissan.—This paper also will appear in *extenso*.

On Stereochemistry.—C. Friedel.—A reply to M. Colson's paper (*Comptes Rendus*, cxvi., p. 994). The author contends that M. Colson does not attack stereochemistry as recognised by its upholders, but certain inexact ideas of his own, and that he has failed to understand the abbreviated formula of van 't Hoff.

Diazoamidobenzene and Paradiazoamidotoluene Benzoates, and Metanitrobenzoates.—A. Haller and A. Guyot.—The authors have employed the method of Knœvenagel (*Berichte*, xxiii., p. 2957) for obtaining solid diazobenzene chloride, sulphate, and nitrate. This method consists in treating an alcoholic solution of a mixture of amine and of organic acid with amyl nitrite and isolating the precipitation. In this manner they have obtained diazoamidobenzene benzoate, diazoamidobenzene metanitrobenzoate, paradiazoamidotoluene benzoate, and paradiazoamidotoluene metanitrobenzoate. Attempts to obtain diazoamidobenzene acetate, formiate, and orthotoluuate, have not proved successful, the result being always pure, crystalline diazoamidobenzene. The authors have also tried the action of amyl nitrite upon a mixture of ethyl cyanacetate or acetylacetate and of paratoluidine. In both cases the sole product was diazoamidotoluene.

New System of Atomic Weights founded in part on the Direct Determination of the Molecular Weights.—A. Leduc.—The system of atomic weights generally adopted includes among its fundamental determinations that of the composition of potassium chlorate, which gives room for doubt. The author has recently shown that the atomic weight of oxygen is 15.88, the density of this gas with reference to air being 1.10503, and that of nitrogen 0.97203. He has more recently established that the molecular volume of carbon monoxide, with reference to oxygen under normal conditions, is close upon 1.0001. Hence we are led to admit that nitrogen and carbon monoxide, by reason of the proximity of their critical points, have the same molecular volume within about 1-10,000th part. Hence the atomic weight

of nitrogen is $15.88 \times \frac{0.97203}{1.10503} \times 1.10001 = 13.97$. The determinations of Stas lead to the value 13.94. According to the author's experiments $\text{NO}_3 = 61.61$, and consequently $\text{Ag} = 107.17$. He finds for Cl the value 35.21, for Br 79.39, and for I 125.96. He finds for carbon the atomic weight 11.916.

Decomposition of Alkaline Aluminates by Carbonic Acid.—A. Ditte.—A current of carbonic acid passed into a solution of an alkaline aluminate containing an excess of alkali will give different results according to the magnitude of this excess, so that we may have or fail to have crystals of hydrated alumina. If the liquid is rich in alumina and poor in alkali, crystals are quickly formed. With a solution rich in alumina and poor in aluminate we may obtain merely a precipitate of the double carbonate.

Mixtures of Ether and Water.—L. Marchis.—The vapour tension of a mixture of ether and water is independent of the composition of the liquid, provided that we have a solution of water in the ether or a mixture formed of two strata.

Formation-Heat of Arragonite.—H. Le Chatelier.—The author finds the heat of the transformation of arragonite into calcite -0.3 cal.

Ammoniacal Fermentation of Soil.—A. Muntz and H. Coudon.—The formation of ammonia in the soil which is observed, especially after the use of organic manures, is due to the intervention of lower organisms and not to a chemical action. The organisms which produce this transformation appear to be numerous.

Composition of the Salts employed as a Condiment by the Population near the Oubangui.—J. Dybowski and Demoussy.—The tribes concerned use as a condiment to their food saline matter, composed of potassium chloride, sulphate, and carbonate, and containing no sodium. It is obtained by lixiviating the ashes of certain plants, ferns, aroids, gramineæ, and polygonaceæ. It results that potassium chloride and sulphate may be ingested with impunity in considerable quantity.

Oxyhæmatine, Reduced Hæmatine, and Hemochromogen.—H. Bertin-Sans and J. Moitessier.—The authors show that by the direct action of reducing agents upon alkaline (not ammoniacal) solutions of pure oxyhæmatine there is formed not hæmochromogen, but a compound with a special spectrum, which they propose to name reduced hæmatine. This compound yields secondarily hæmochromogen, by the action of ammonia, of amines, and of albumenoids.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. ix. and x., No. 1, January 5, 1893.

Determination of Extract left on the Evaporation of Wine.—J. A. Müller.—The author determines the weight of the dry extract left on the evaporation of a wine at 100° , and the extract left on evaporation in a dry vacuum.

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Testing for Cotton in Woollen Goods.—What is the chemical used for testing woollen material to see if cotton is mixed with it? The test that I have seen takes away every partial wool and leaves cotton warp behind.—F.S.C.

Aluminum Sulphide.—Will the correspondent who wrote for information regarding aluminum sulphide some time ago from Hotel Metropole, Brighton, write again, as that address is unknown?—H. N. WARREN, 18, Albion Street, Liverpool.

MEETINGS FOR THE WEEK.

- MONDAY, 13th.—Medical, 8.30.
Society of Arts, 5. "Alloys," by Prof. W. Chandler Roberts-Austen, C.B., F.R.S. (Cantor Lectures).
TUESDAY, 14th.—Institute of Civil Engineers, 8.
Royal Institution, 3. "Physical and Psychological Neurology," by Prof. Victor Horsley, F.R.S.
Photographic, 8.
Royal Medical and Chirurgical, 8.30.
WEDNESDAY, 15th.—Society of Arts, 8. "Technical Education—its Progress and Prospects," by Sir Philip Magnus.
Meteorological, 7.
Microscopical, 8.
THURSDAY, 16th.—Royal, 4.30.
Royal Society Club, 6.30.
Royal Institution, 3. "The Great Revival—A Study in Mediæval History," by the Rev. Augustus Jessopp, D.D.
Chemical, 8. "Limits of Accuracy of Gold-Bullion Assay and the Losses of Gold Incidental to it," by T. K. Rose. "Boiling-point of Liquid Nitrous Oxide at Atmospheric Pressure, and on the Melting-point of Solid Nitrous Oxide," by W. Ramsay, F.R.S., and John Shields, Ph.D. "Isomerism of Aliphatic Aldoximes," by W. R. Dunstan and T. Dymond. "Formic Aldoxime," by W. R. Dunstan. "Properties of α -Benzaldoxime," by W. R. Dunstan and M. C. Luxmore.
FRIDAY, 17th.—Royal Institution, 9. "Ancient Egyptian Pigments," by W. J. Russell, F.R.S.
Quckett Club, 8.
SATURDAY, 18th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

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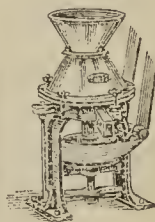
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THE CHEMICAL NEWS.

VOL. LXVII., No. 1738.

ESTIMATION OF UREA.

By WALTER COLQUHOUN, M.A.

DISSATISFIED with the inaccuracy and the labour involved in the methods of estimating urea for clinical purposes at present in vogue, I was led to devise the arrangement which I describe.

My apparatus consists of a burette, B, graduated from the stopcock, s_1 , to show tenths of a c.c., and attached by a piece of indiarubber tubing to a tube, T, carrying two side tubes, as shown in the drawing, and widened at A to hold about 15 c.c. between the lower side tube and the stopcock s_2 . Below the stopcock s_2 the tube is widened to a bulb, C, which holds about 6 c.c., and a stopcock, s_3 , is placed below the bulb. The side tubes are connected by indiarubber tubing with reservoir R_1 and R_2 , of which R_1 holds water and R_2 sodium hypobromite or hypochlorite. As the reservoir R_2 is not moved, the indiarubber tubing may, in its case, be replaced by glass tubing and a stopcock. Clips are placed on the indiarubber tubing to control the flow of the fluid in the reservoirs, and the apparatus is mounted on a suitable stand with rests for the reservoirs. It is worked as follows:—

The stopcock s_2 is withdrawn, and the stopcock s_3 having been closed, a measured quantity of urine is introduced into the bulb C by means of a pipette curved at the delivery end, so that it may be inserted into the hole leading from the stopcock s_2 to the bulb. The stopcock s_2 is then replaced, and water is run in from the reservoir R_1 until it rises above the hole in the stopcock, which is then shut. Sodium hypobromite is then run in to the desired amount from the reservoir R_2 , and water is then run in from R_1 to fill the burette, the stopcock s_1 being then closed.

On now opening s_2 nitrogen is evolved, and atmospheric pressure may be maintained by holding R_1 at the proper level, taking care that the clip on the tube leading to R_1 is open. After reading the amount of nitrogen s_1 is opened, and then s_2 , and the apparatus rinsed out with water from R_1 , when it is ready for another estimation.

To do away with repeated corrections for temperature, pressure, and tension of aqueous vapour, I introduce by means of my pipette, which is graduated on the stem and can measure to 1-100th of a c.c., the amounts of urine given in the following table, which are calculated so that the quantity given under a certain temperature and pressure evolves as many c.c. of nitrogen as the urine contains grms. of urea per litre, or weighed grains per thousand measured grains.

The table is given for rises in pressure of 10 m.m. and in temperature of 5° F., but the differences are so constant that it is easy to interpolate for intervening temperatures and pressures.

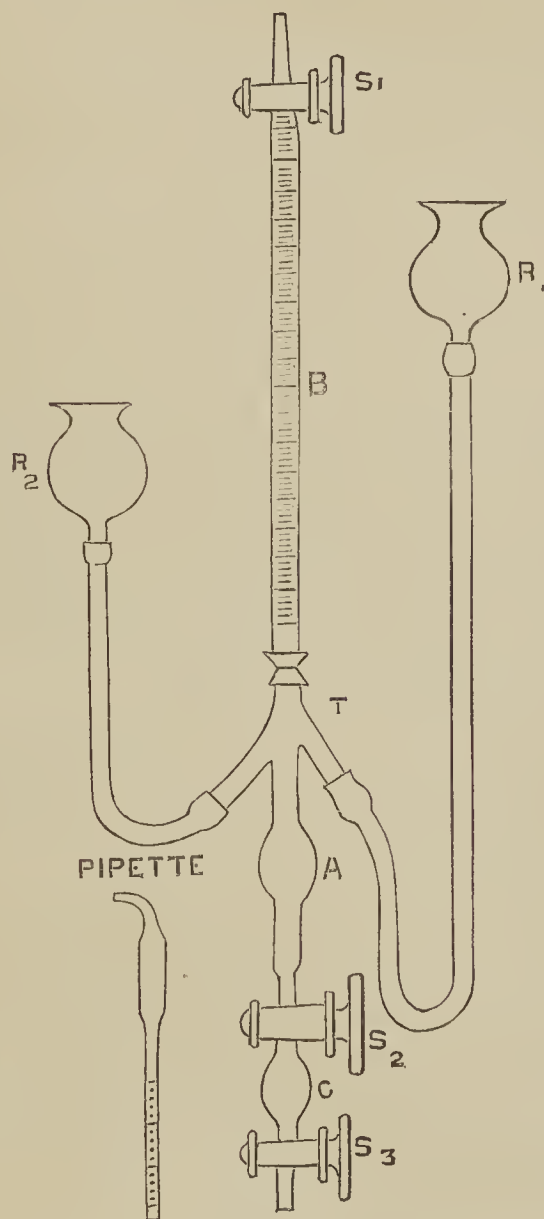
My apparatus is an improved form of Russell and West's, but even those who prefer to use Apjohn's apparatus, or Dupré's modification of it, would find it an advantage to use the measurements given in the above table, or preferably to use, as I did in my experiments, double the quantities given, so that every 2 c.c. of nitrogen count one part of urea per thousand. My experiments were made with an apparatus double the size of that described, and the results may be briefly stated as follows:—

I. Using sodium hypobromite prepared according to Russell and West's directions, and the quantities of fluid given in the table, which is calculated for an evolution of 92 per cent of N, the results equal in accuracy those of any other chemical analysis under ordinary conditions.

2. The water and hypobromite used should be allowed to gain the temperature of the laboratory before using, and on no account should heat be applied unless time be afterwards given for the apparatus to cool down to the surrounding temperature. It is quicker and more accurate to let the action take place in the cold.

3. There is no tendency to re-absorption of the N, as is seen from the details of my experiments, in most of which readings were taken at the end of twenty-four hours.

4. The hypobromite should not be added too quickly. In the apparatus which I found to work best, the hole in the stopcock s_2 is one-quarter inch in diameter.



I have made about thirty estimations with my apparatus with solutions of urea of known strength at temperatures varying from 50° F. to 65° F. In each case I took double the amount of fluid given in the table, and I give details of a few estimations to show my method of working.

2 per cent Solution.

I.—Temperature 55° F.; Pressure 29.7 in.;

5.46 c.c. taken.

N evolved at end of 20 minutes 40 c.c. = 2 per cent urea.

" " " 24 hours 40.3 " = 2.015 " "

1.8 per cent Solution.

II.—Temperature 50° F.; Pressure 29.7 in.;

5.53 c.c. taken.

N evolved at end of 10 minutes 35.8 c.c. = 1.79 p.c. urea.

" " " 1 hour 36 " = 1.8 " "

" " " 24 hours 36 " = 1.8 " "

					Pressures.								
Inches	28'35	28'74	29'14	29'53	29'92	30'31	30'71	31'10	31'49
Millimetres	720	730	740	750	760	770	780	790	800
40° F.	2'700	2'738	2'776	2'814	2'852	2'889	2'927	2'965	3'003
45° F.	2'669	2'706	2'743	2'781	2'818	2'856	2'893	2'930	2'968
50° F.	2'636	2'673	2'710	2'747	2'784	2'822	2'859	2'896	2'933
55° F.	2'604	2'640	2'677	2'714	2'751	2'788	2'824	2'861	2'898
60° F.	2'571	2'607	2'644	2'680	2'716	2'753	2'789	2'826	2'862
65° F.	2'537	2'573	2'609	2'646	2'681	2'717	2'753	2'790	2'826
70° F.	2'503	2'538	2'574	2'610	2'646	2'681	2'717	2'753	2'788
75° F.	2'468	2'503	2'538	2'574	2'609	2'644	2'680	2'715	2'750
80° F.	2'431	2'466	2'501	2'536	2'571	2'606	2'641	2'676	2'711

2 per cent Solution.

III.—Temperature 60° F.; Pressure 29'5 in.;
5'36 c.c. taken.

N evolved at end of 20 minutes 39'8 c.c. = 1'99 p.c. urea.
" " " 24 hours 39'95 c.c. = 1'997 " "

1 per cent Solution.

IV.—Temperature 55° F.; Pressure 29'2 in.;
5'37 c.c. taken.

N evolved at end of 20 minutes 20 c.c. = 1 p.c. urea.
" " " 24 hours 20'1 " = 1'005 " "

My maximum deviation from accuracy was an excess of four-tenths of a c.c. on 36 c.c. of nitrogen, which gives 1'82 per cent urea instead of 1'8 per cent, and it would appear since my deviations were nearly all errors of excess, that under my conditions the urea gives up on long standing from 92 to 92'7 per cent of nitrogen. I preferred to calculate my table for an evolution of 92 per cent, because if the tube be tapped to dislodge any bubbles of gas which may adhere to the sides and to start small bubbles to the surface, the reading at the end of twenty minutes is almost accurate.

My maximum error was slight in comparison with the errors which may arise owing to neglect of corrections for temperature, pressure, and tension of aqueous vapour. Thus, if at the extreme temperatures and pressures of the table the number of c.c. given for 60° F. and 760 m.m. were taken, the error would amount to 0'2 per cent, or 0'23 per cent of urea on a 2 per cent solution.

I think I may claim to have reduced manipulation and calculation to a minimum with my arrangement, which at the same time gives perfectly reliable results. The measurement and introduction of the urine, the opening and shutting of stopcocks, and a reading at the end of twenty minutes is all that is demanded from the experimenter. Another opening of stopcocks washes out the apparatus, which is then ready for another analysis.

Mr. Otto Muller, 175A, West George Street, Glasgow, has been authorised to supply the apparatus.

67, Gibson Street, Hillhead, Glasgow.

ON THE PREPARATION OF URANIUM AT A HIGH TEMPERATURE.

By HENRI MOISSAN.

OF late years metallurgy has utilised powerful currents for producing electrolyses. The new preparations of magnesium and aluminium are instances, but we consider that the heat produced by the electric arc may also be especially utilised when it is required to reduce with carbon certain oxides hitherto regarded as not capable of reduction.

Thus the use of the electric furnace enables us quickly to prepare the refractory metals, which hitherto could be obtained only with difficulty, or not at all.

It is merely needful to place in the cavity of a furnace

of lime a certain quantity of magnesium, which is absolutely stable at the highest temperatures of the arc, and to arrange above it a crucible of retort-coke containing the mixture of carbon and oxide to be reduced.

If the metal is volatile, we cause the furnace to be traversed by a current of hydrogen and the metallic vapours are condensed in a refrigerated receiver. In this manner we prepare calcium, barium, and strontium. If the metal is not appreciably volatile, it remains at the bottom of the crucible in the form of an ingot. This is the case with uranium, the preparation of which we are about to describe.

Metallic uranium had been obtained by Peligot in very small quantities and with great difficulty by reducing uranium oxide with an alkaline metal. At ordinary temperatures the uranium oxides are not reducible by carbon. It is not the same, as I have already intimated, at the high temperatures which we can apply in the electric furnace.

To obtain this metal we ignite, in a porcelain capsule, uranium nitrate, which may be prepared in a state of great purity. There remains a reddish mixture of uranium sesquioxide and of the green oxide U_3O_4 . We add to this mixture a slight excess of charcoal in powder, and the whole is strongly compressed into a coke crucible. On submitting this mixture, in the electric furnace, to the action of the arc produced by a current of 450 ampères and 60 volts the reduction is completed in a few moments. After cooling, we extract from the crucible a metallic ingot of a brilliant fracture and of great hardness, which if thrown upon porcelain, or if its fragments are agitated in a glass bottle gives brilliant sparks from the combustion of traces of the substances. There occurs—though with far greater lustre—a phenomenon analogous to the combustion of particles of iron which take fire by simple friction in the air.

The yield of uranium by this process conducted in the electric furnace is very great. An experiment lasting twelve minutes yielded a regulus of from 200 to 220 grms. The 600 grms. which I have the honour of presenting to the Academy have been prepared in these operations, each reduction requiring only about ten minutes.

This sample does not consist of pure uranium.* It is a true cast-metal, and its proportion of carbon varies with the predominance, whether of the oxide or of the coke in the mixture.

A qualitative examination showed that merely uranium and carbon were present.

Determinations of different specimens of this uranium carbide gave the following results:—

		I.	II.	III.	IV.
U	86'25	89'46	89'10	95'70
C	13'50	11'03	10'24	5'02

* A rather large number of metals have never been obtained in a state of perfect purity: some contain carbon, silicon, or the alkaline metals. We know now that a very small quantity of these impurities may modify the physical and even the chemical properties of these elementary bodies. To us it seems important to determine with care the state of purity of the metals obtained by means of the electric furnace.

We add that these uranium carbides slowly decompose water at the ordinary temperature—a property to which we shall have occasion to revert—and that their melting point is much higher than that of platinum.

In fine, we have obtained a true cast-uranium at a high temperature by the direct reduction of the oxides of uranium by coke. In a future research we shall give the characteristic properties of this compound, and indicate how it may be refined and what are the properties of the pure metal.—*Comptes Rendus*, cxvi., No. 8.

THE DETECTION AND DETERMINATION OF ARSENIC.*

By JOH. THIELE.

1. Hypophosphorous Acid as a Reagent for Arsenic.

It has already been observed that arsenic is precipitated in a metallic state on prolonged ebullition with hypophosphorous acid. According to Thiele this reduction may be effected without evaporative boiling in a hydrochloric solution and with hypophosphorous acid which is not highly concentrated. By means of this reaction arsenic may be rapidly and conveniently detected even in presence of antimony and tin.

For this purpose the solution containing arsenious or arsenic acid is strongly acidified with hydrochloric acid, and to every 10 c.c. of the liquid there is added at least 1 gram. commercial sodium hypophosphite. On heating for some time on the water-bath the arsenic falls as a brown or blackish brown powder. If the liquid is very dilute it must be heated for a considerable time up to thirty minutes. If the amount of arsenic present is very small, the precipitate does not subside, but the liquid takes a brownish colour, which is especially visible if it is regarded obliquely downwards. In a sulphuric solution and in the absence of a hydracid the reduction takes place either not at all or very imperfectly. Hence it seems not to be an oxygen compound of arsenic but arsenic chloride, which is reduced by hypophosphorous acid. According to Thiele, arsenic iodide is still more easily reduced than arsenic chloride, so that an addition of potassium iodide or hydriodic acid expedites the reaction and renders it more sensitive. Whilst in the absence of potassium iodide 0.05 gram. arsenious acid is necessary to occasion a brownish reflexion in from 5 to 10 c.c. of liquid, 0.025 gram. is sufficient on the addition of a small crystal of potassium iodide.

Saving the precious metals which are likewise reduced by hypophosphorous acid, the presence of copper only absolutely interferes with the reaction, as this metal is precipitated even from a very dilute solution of the same colour as arsenic. Arsenic and bismuth are precipitated only from very concentrated solutions, but the precipitation is incomplete whether with or without the addition of potassium iodide. The precipitates given by these metals are distinguished from that of arsenic by their black colour. If the colour of the precipitate renders it probable that one of the two metals is present, the deposit is placed upon a small filter, and without washing it is taken up with a few drops of bromine in hydrochloric acid. From this solution, on repeating the reduction, the arsenic alone is deposited with its characteristic colour. In presence of antimony and bismuth—the latter especially—the addition of potassium iodide may be advantageously omitted, since the intense yellow colour occasioned by the iodides of these metals interferes with the sensitiveness of the reaction. From the same reason in the presence of large proportions of iron the air must be excluded as far as possible from the reduced and decolourised liquid to prevent the formation of iron chloride.

For the quantitative determination of iron and its separation from antimony and tin, the process with sodium hypophosphite seems unsuitable, as the arsenical deposit is extremely readily oxidised and cannot be washed.

2. On the Use of the Marsh Apparatus for Detecting Arsenic in Presence of Antimony.

By occasion of an investigation of Tookey's process for the separation of antimony and tin, Thiele inquired whether during the precipitation of antimony by iron any loss occurs by the formation of antimony hydride, and he found that in accordance with earlier observations, solutions of antimony do not evolve stibine with iron and hydrochloric acid and iron. As arsenic hydride is evolved from arsenical compounds under similar conditions, this process would afford a means of recognising arsenic in presence of antimony. But for this purpose only iron can be suitable which is free or approximately free from sulphur, since the presence of sulphur may entirely prevent the recognition of small quantities of iron in consequence of the formation of hydrogen sulphide. The production of such iron was connected with unexpected difficulties. The author succeeded only after a number of experiments in obtaining an iron electrolytically which contained merely a minimum of sulphur.

For its preparation 200 grms. commercial ferrous chloride, free from water of crystallisation, was dissolved in 500 c.c. of water, digested persistently in heat with the purest possible iron from former operations in order to remove any electro-negative metals which might be present, and mixed with barium chloride in order to remove sulphuric acid.

The filtrate, after the addition of 25 c.c. of glacial acetic acid, was submitted to electrolysis by means of a Bunsen element. The negative electrode consisted of a sheet of platinum, and the positive electrode of a plate of the purest iron procurable. As the impurities of the latter are deposited at the bottom in the form of a black mud, the piece of platinum must terminate 2 c.m. above the bottom of the vessel, so that it may not come in contact with the latter.

In order to prevent the oxidation of the solution of ferrous chloride by the oxygen of the air, the decomposition cell was placed in a glass cup containing a little water and covered with a glass ball. The polar wires are carried up through the water in the decomposing cell. They do not require insulation on account of the low conductivity of pure water. With one Bunsen element and a polar surface of 100 square c.m., 2 grms. iron may be deposited hourly. The solution of chloride may be repeatedly used after the addition of some acetic acid.

The iron obtained in this manner must be at once rinsed with water, alcohol, and ether, and dried *in vacuo* over sulphuric acid. If this iron is used in a Marsh apparatus with dilute hydrochloric acid as developing liquid, it yielded no mirror of arsenic or antimony, whether alone or after addition of a considerable quantity of pure antimony chloride. The gas was passed through a layer of wadding 10 c.m. in length. After an addition of arsenic or arsenious acid there appeared at once a copious formation of arsine.

In a quantitative experiment the apparatus was charged with iron and hydrochloric acid, and a weighed quantity (0.16 gram.) of arsenious acid. Hereby, however, only 10 per cent of the existing arsenic was converted into arsine and recovered as arsine, whilst copious black flocks of arsenic remained behind in the developing vessel.

An experiment undertaken in the same manner with non-platinised zinc and hydrochloric acid gave about 94 per cent of the arsenic present as arsine. Here also arsenic remained in the gas generator after the completion of the experiment.

This difference in the behaviour of zinc and iron,

* From the *Zeit. Anal. Chemi*

according to the further experiments by the author, is to be explained by the circumstance that iron evolves arsine less readily from the precipitated arsenic than does zinc. Hence the detection of arsenic with iron is much less sensitive and succeeds only down to 0.1 or 0.15 m.grm.

The sensitiveness of the reaction is considerably increased if antimony chloride is simultaneously introduced into the apparatus. It is then easily practicable to detect 0.015 m.grm. arsenic in whatever state of oxidation it may be present.

The reaction certainly requires a longer time than the use of zinc, about two hours. Lest the development of hydrogen should become too violent, the solution of antimony (2 to 3 c.c. of a concentrated solution of oxychloride in hydrochloric acid of specific gravity 1.124), are added gradually.

Tin ranks intermediately in its behaviour between zinc and iron, as it is only able to evolve stibine in traces.

(To be continued).

SOLID AIR.

PROFESSOR DEWAR communicated to the Royal Society at its meeting on Thursday, March 9, a most interesting development of his experiments upon air at very low temperatures. Our readers are already familiar with the fact that he has liquefied air at ordinary atmospheric pressure. He has now succeeded in freezing it into a clear, transparent solid. The precise nature of this solid is at present doubtful, and can be settled only by further research. It may be a jelly of solid nitrogen containing liquid oxygen, much as calves' foot jelly contains water diffused in solid gelatin. Or it may be a true ice of liquid air, in which both oxygen and nitrogen exist in the solid form. The doubt arises from the fact that Prof. Dewar has not been able by his utmost efforts to solidify pure oxygen, which, unlike other gases, resists the cold produced by its own evaporation under the air pump. Nitrogen, on the other hand, can be frozen with comparative ease. It has already been proved that in the evaporation of liquid air nitrogen boils off first. Consequently the liquid is continually becoming richer in that constituent which has hitherto resisted solidification. It thus becomes a question whether the cold produced is sufficiently great to solidify oxygen, or whether its mixture with nitrogen raises its freezing-point, or whether it is not really frozen at all, but merely entangled among the particles of solid nitrogen, like the rose-water in cold cream. The result, whatever may be its precise nature, has been attained by use of the most powerful appliances at command—a double set of the vacuum screens already described in our columns, combined with two powerful air pumps. Upon either view of its constitution, the new solid is in the highest degree interesting and hopeful.—*Times*.

GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 116).

Our First Series of Syntheses.

IN our original intention was to set up as close an imitation of Dumas's apparatus as we might be able to construct, and, by means of it, to carry out a few syntheses exactly in his style in order to fortify our position as critics of his work, and, in the most direct manner possible, to decide the important question whether he really had, as we suspected, forgotten to reduce his water-weights to the vacuum. But we soon came to give up

this idea, for this reason amongst others, that we had not a high-class air-pump at our disposal, and *without such an instrument we thought at the time* we should not be able to weigh our oxide of copper and metallic copper *in vacuo*, as he did. We had to modify Dumas's method so as to bring it within the range of our resources, and this being so, we thought we might as well try and improve upon it by utilising our method for the production of absolutely oxygen (*i.e.*, O₂) free hydrogen, and by working on a smaller scale. We were, and to this day are, convinced that Dumas positively lost precision by working with such extraordinarily large quantities of oxide of copper, that he had to execute his final weighings after having become exhausted by "from fifteen to twenty hours" of continuous work. We have no doubt in our own minds that our results are at least as close approximations to the truth as his, although we worked on such a small scale that we were able to carry out all our weighings with a balance of only "100 grms. carrying power" (the actual charge, it is true, sometimes rose to 120–130 grms.), and were able to complete a synthesis without working longer than from about nine in the morning to five to six in the evening. Dumas tells us that his nineteen published experiments correspond to no less than forty to fifty such experiments actually made, which means about one failure for every two attempts. Of the thirteen actual syntheses which we made, only *one* was a breakdown, and *one* other had to be rejected on account of unobserved blunders.

For the production of the necessary continuous supplies of hydrogen we used two "Kipps," which were coupled together by means of one of those admirable two-way cock arrangements of Messrs. Greiner and Friedrichs, so that we were able to use either one or the other, and, supposing one to be exhausted, to re-charge it while the other was working. Let us add at once that we never had occasion to do this. In a few of the first trials (with small quantities of oxide of copper) we used 10 per cent hydrochloric acid for liberating the gas, but all the later experiments were made with 20 per cent sulphuric acid. For the purification of the gas we used at first to pass it successfully through, (1) cotton-wool; (2) a U-tube charged with vitrioled pumice; (3) a combustion tube 370 m.m. long and 15 m.m. wide inside, containing as thick a closely-wound spiral of fine copper gauze as it would hold, and drawn out at each end to avoid the use of corks. This tube was kept at a red heat during the progress of an experiment, and served to eliminate the antimony, arsenic, and sulphur which the gas contained, besides converting the oxygen of the unavoidable trace of air into water, which latter was caught in a U-tube charged with vitrioled pumice attached to the outlet. The principal impurity in our zinc was antimony; we therefore, in our later experiments, purified our gas by sending it from the "Kipp" direct into a large tower (210 m.m. high and 35 m.m. wide), filled with fragments of caustic soda, which converted almost the whole of the antimoniuiretted hydrogen into a black deposit of SbOH. From the soda-tower the gas passed into the tube containing red-hot copper.

The Oxide of Copper was prepared from chemically pure copper foil by cutting it up, placing it in a Berlin basin, and, in it, heating it in a muffle for a day or two. The muffle was new, and, during the progress of the research was never used for any other work. The only impurity which the oxide could have contained is sulphur (from the gas-flames); we therefore tested about 10 grms. of it by treating it with pure fuming nitric acid, &c., and searching for sulphuric acid by means of chloride of barium. From the whole of the 10 grms. of oxide used only a barely visible trace of a precipitate was obtained, which amounted to no more than the one seen in the "blank" which accompanied the experiment proper. Oxide of copper produced in the way described never contains the full proportion of oxygen demanded by the formula CuO, but this does not matter; over the oxide

* *Proceedings of the Philosophical Society of Glasgow.*

produced by heating the nitrate it offers the inestimable advantage of not being hygroscopic. When we had used up the first supply of oxide, the metal obtained from it was re-oxidised in the muffle, which took far less time than the oxidation of the original compact metal.

Our apparatus is represented in the Figs. 3.1, 3.2, 4 and 5.

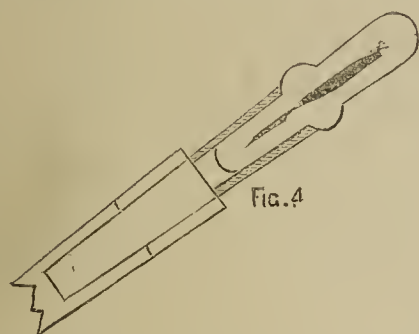


Fig. 4

The reduction-tube, L, was made out of a piece of wide combustion-tubing. When used, it was heated in a magnesia-bath by means of a set of Bunsens, a roof-shaped chimney made of asbestos pasteboard serving to reflect down the heat on the top part of the tube. In the original apparatus this tube was connected with the outlet of the preceding vitriol-tube by means of an india-rubber stopper, which, as we may state, was taken out before the apparatus went to the balance. But we subsequently discarded the stopper and substituted for it the arrangement shown more clearly in Fig. 5, for the explanation of which it suffices to state that the joints at K and *k'* were made tight by means of strips of warm non-vulcanised sheet india-rubber wound round and secured by wire ligatures on both sides.

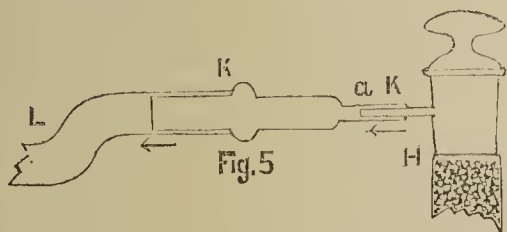


Fig. 5

The water-receptacle, P, was made out of a fractionating flask. Fig. 3.2 shows its construction and mode of connection with the reduction-tube. The tube, *d*, is fixed in its place by means of a cork, *g*, which terminates a little below the edge of the neck of the flask so as to form a cup, which is filled completely with sealing-wax so as to avoid contact between air and cork. The outlet of the reduction-tube O, in Fig. 3.1, and, *a*, in Fig. 3.2, projects into the tube *d*, the joint at *b* being made tight by means of a wired-on band of black sheet india-rubber, as in the case of the improved form of the reduction tube entrance. After a few experiments had been made with the apparatus as described, we found that, sometimes, a sublimate of water settled down in the annular space between *d* and *a*. To prevent this inconvenience, we provided the arrangement represented in Fig. 6. H is the last drying-tube preceding the reduction-tube. The original intention was to close the stopcock, *b*, whenever a sublimate of water shows itself between *a* and *d*, and let the gas go through the side-tube, *c d e f*. But we subsequently found it easy to adjust the cocks *b* and *d*, so that a small portion of the hydrogen went constantly through the side-tube and swept down any steam present within that annular space that might otherwise have condensed into a sublimate of water.

The weighings were effected by means of that very excellent Oertling's "14-inch," which one of us described in the *Zeit. für Instrumentenkunde* some years ago, and a set of iridio-platinum weights from Johnson, Matthey, and Co., which were adjusted by Oertling, and subse-

quently readjusted by one of us (W.D.), with the co-operation of his then assistant, Mr. Barbour. To reduce the uncertainties of the weighings to a minimum, the several portions of the apparatus were tared with somewhat lighter similar apparatus of as nearly as possible the same displacement, so that the weight standards lying on the pan represented little more than the net weight to be determined.

In the execution of the syntheses the exact *modus operandi* was not always exactly the same. Little improvements were introduced as our experience expanded, but there would be no use in here giving the history of our apprenticeship; it suffices to describe the *modus operandi* in its latest form, which, indeed, was employed in all the actual syntheses intended for the calculation of the value $H_2 : O$.

The first step in each case was to start the hydrogen and let it go through the purifiers, the copper tube being meanwhile kept at the ordinary temperature. The reduction-tube was then charged with a suitable quantity of oxide of copper, and prepared for the balance by heating the oxide in a current of vitriol-dried air, until every trace of moisture was sure to be expelled. The tube was

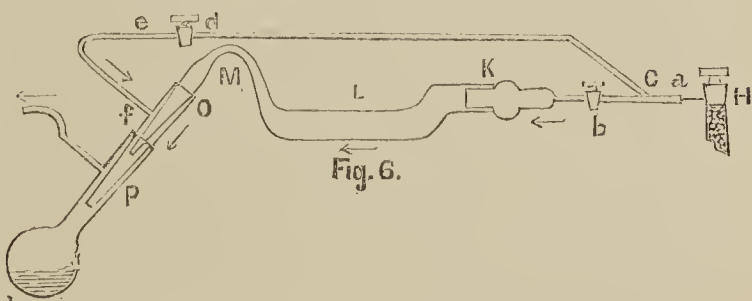


Fig. 6.

then allowed to cool in dry air, closed at both ends, and next kept immersed in a water-bath of the temperature of the balance room, beside the tare tube, until both could be assumed to have acquired that temperature. The two portions of the apparatus were then taken out of the bath, wiped dry with a towel, and suspended at the balance, the working tube at the left end and the tare tube at the right, a special tare equal in weight to the stopper and cap on the working tube being placed in the right pan. After some time the working tube was opened for a second to bring its atmosphere to the pressure of the air outside, and equilibrium established by means of weights. Some ten minutes later the weights were re-adjusted, and this operation was repeated until the state of equilibrium had become permanent, which always was the case after a short time—thanks chiefly to the water-bath which had established equilibrium of temperature. At the end, the cap and stopper were removed from the working tube, and the corresponding tare from the right pan, and the balance made to vibrate two or three times to obtain the exact value of the weight to be determined. A similar method was used for the water receptacle and the U-tubes, which were tared next. During one of the periods of rest involved in the tarings, the gas lamp under the copper wire gauze tube was lighted, and the hydrogen allowed to stream through the hot tube till all the oxygen and moisture of the gauze could be assumed to be removed. Only then the vitriol tube H was attached to the end of the copper gauze tube, and the apparatus thus made ready for the joining on of the reduction-tube and the water receptacle. The outlet of the last U-tube S had a long india-rubber tube attached to it, so that any gas that streamed out there could be collected over water in a graduated Pisani bottle (Fig. 1) provided for the purpose. The joints between P and R, and between R and S, were made with best india-rubber tubing in such a way that the two glass tube ends within the india-rubber almost touched each other, and the joint secured on both sides by ligatures of copper wire.

(To be continued).

A VOLUMETRIC METHOD FOR THE
DETERMINATION OF LEAD.*

By F. C. KNIGHT.

A TECHNICAL method for the volumetric determination of lead, requiring but an ordinary amount of manipulation and occupying a short space of time, has long been desired. A number of such methods have been suggested from time to time that promised more or less success. Of these there are but two which give results that are sufficiently accurate even for technical work, a brief outline of which will be given.

The first, which is the more practical, consists of neutralising the nitrate of lead solution with ammonia or carbonate of ammonia, then adding an excess of acetate of sodium, and effecting the titration with a standardised solution of bichromate of potassium, the end reaction being indicated by a red colouration on bringing a drop of the lead solution in contact with a drop of a neutral solution of nitrate of silver. With careful manipulation this process yields good results. The greatest objection to be brought against the method is the uncertainty of the complete precipitation of the lead as the chromate if special precautions are not observed; the length of time involved in the process, and, finally, the ease with which the end-point of the reaction can be overstepped.

The other method consists in precipitating the lead as carbonate from its solution, dissolving the precipitate in a measured quantity of normal nitric acid, to which then a neutral solution of sulphate of sodium is added. The sulphate of lead is precipitated and an equivalent amount of nitrate of sodium formed. The free nitric acid is subsequently determined with a normal alkali solution, the lead percentage being calculated from the observed difference between the original amount of nitric acid used and that found to be still free. This plan requires the lead solution to be quite free from other elements, for which special precautions are necessary, and the length of time involved in the operations quite unfits the process for technical laboratories.

There is another method which has been lately described, which, while not volumetric, appears to offer great advantages over the preceding ones. It consists in dissolving the sulphate of lead in an ammonium chloride solution, and precipitating the lead from the same in the metallic form by means of sheet aluminum, the lead finally being weighed. The results appear to be very accurate. The existing prejudice in technical laboratories against any method which involves a gravimetric determination will, however, operate as a bar against its general introduction if a method equally as accurate, or sufficiently so for all purposes, but volumetric, can be found.

The method about to be described is offered in the hope that it will meet the required conditions. It is based on the formation of oxalate of lead, the decomposition of this salt by sulphuric acid, the determination of the liberated oxalic acid by permanganate of potassium solution, and the calculation of the lead percentage from the amount of oxalic acid with which it was originally combined.

It is not claimed that the idea on which this scheme is founded is new: in fact, a method along similar lines was proposed by Hempel, it being also stated by him that the results obtained were not absolutely accurate owing to the solubility of the oxalate of lead, which error, however, could be reduced to within the limits of 1 per cent by careful manipulation.

Fresenius, in discussing the solubility of oxalate of lead in water, states it to be distinctly greater than that of sulphate of lead, the solubility being still further increased by the presence of ammonia and ammonium salts.

A large number of experiments, instituted for the pur-

pose of determining how the solubility of the oxalate of lead in water could be overcome, showed eventually that while it could not be entirely nullified, it could be reduced to its minimum by effecting the precipitation from an aqueous solution of the lead salt containing about an equal bulk of 95 per cent alcohol, only the slightest traces of lead remaining in solution under such a condition. Further experiments demonstrated that the precipitation was equally complete in the presence of free acetic acid which had been added to the alcoholic solution.

To a neutral solution of nitrate of lead measuring about 20 c.c., an equal volume of 95 per cent alcohol and 5 c.c. strong acetic acid were added, and the lead precipitated by oxalic acid. The precipitate was filtered, well washed with hot water, and the filtrate saturated with hydrogen sulphide gas. A slight brown colouration was noticed in the course of time, but a precipitate of sulphide of lead failed to appear even after the solution had stood for several days.

This experiment was repeated a number of times with the same result, giving thus the assurance that the error due to the excessively slight solubility of the oxalate of lead, under conditions formulated, would not act as a disqualification of a technical method which was based on its use.

The oxalate of lead precipitated from cold alcoholic solutions comes down as a heavy white flocculent precipitate, which settles quickly on agitating the solution either by stirring or shaking, leaving the supernatant liquid perfectly clear. From heated solutions the precipitate falls as a brilliant crystalline powder. The composition of the salt is, however, in both cases the same, its formula being PbC_2O_4 , containing 70.18 per cent of lead.

The crystalline precipitate filters rapidly and is easily washed; the flocculent variety becomes reduced in bulk and crystalline on being washed with hot water. It is advisable to precipitate the oxalate from the solution which has been heated to 65° C.

Pure lead having been prepared by reduction from C. P. acetate of lead, freeing the regulus from mechanical impurities, and rolling it into thin sheet lead, varying quantities were weighed out to determine the accuracy of the method under consideration.

The standard of the permanganate of potassium solution containing 1.58 grms. of $KMnO_4$ to the litre was established as follows:—3.65 grms. C. P. crystallised oxalic acid were dissolved in 500 c.c. distilled water, from which three separate portions of 25 c.c. each were taken, 5 c.c. concentrated sulphuric acid added, and the titration performed with the previously prepared permanganate solution. There were used in:—

Experiment.	Oxalic acid. C.c.	Cryst. xalic acid. Grm.	$KMnO_4$, C.c.
1 25	0.1825	58.30
2 25	0.1825	58.35
3 25	0.1825	58.40

Making an average of 58.35 c.c. of permanganate solution used, or 1 c.c. $KMnO_4$ solution = 0.003127 gm. $C_2H_2O_4, 2H_2O$, from which by the simple stoichiometrical calculation, 1 c.c. $KMnO_4$ solution = 0.00513 gm. lead, in the form of oxalate.

The standard being established, a portion of lead was weighed out and dissolved in 3 c.c. concentrated nitric acid, diluted with 10 c.c. hot water, and carbonate of sodium in slight excess added. The precipitate was dissolved by the addition of 5 c.c. strong acetic acid, 20 c.c. of 95 per cent alcohol being then added to the solution. This was heated to 65° C. and the lead precipitated by adding 10 c.c. of a saturated solution of oxalic acid, the precipitate, after settling, being filtered and thoroughly washed with hot water. The lead oxalate was now rinsed from the filter into a beaker, 50 c.c. hot water and 5 c.c. concentrated sulphuric acid added. The solution was warmed to about 65° C., and the titration on the freed

* A Paper read before the Colorado Scientific Society, Nov. 7, 1892. From the *Journal of Analytical and Applied Chemistry*, vi, No. 11.

oxalic acid effected. Ten determinations were made, the results being:—

Exp. No.	Weight of lead taken. Grm.	KMnO ₄ used. C.c.	Weight of lead found.	Per cent obtained.
4.. ..	0.05392	10.4	0.05335	98.94
5.. ..	0.10150	19.7	0.10106	99.56
6.. ..	0.15266	29.7	0.15236	99.80
7.. ..	0.20878	40.6	0.20827	99.75
8.. ..	0.25540	49.7	0.25496	99.82
9.. ..	0.30016	58.5	0.30010	99.97
10.. ..	0.35204	68.6	0.35191	99.96
11.. ..	0.40290	78.4	0.40219	99.82
12.. ..	0.45252	88.2	0.45246	99.98
13.. ..	0.49876	97.1	0.49812	99.89

The average percentage obtained being 99.749.

In order to establish comparisons on a basis which would be of greater value, in that the determinations would be made under conditions necessary in the carrying out of the method on ores and metallurgical products, another series of experiments was instituted, the lead taken for the analysis being brought into the solution, and re-converted into metallic lead, from which point on the process was as above described.

The precipitate of metallic lead from hydrochloric acid solutions was found to be easily, as well as completely, effected by means of pure granulated zinc, the article used having been made by Merk, the granules being of a diameter small enough to allow them to pass through a screen containing 30 meshes to the linear inch. Investigation proved it to be free from lead.

Dilute hydrochloric acid has no action whatever on metallic lead, and even boiling concentrated hydrochloric acid scarcely attacks it. From dilute solutions of pure sulphate of lead in hydrochloric acid granulated zinc precipitates the lead quickly as a sponge, which is easily washed.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 16th, 1893.

Prof. A. CRUM BROWN, F.R.S., in the Chair.

(Concluded from p. 118).

*117. "Electrolysis of Sodid Ethylic Camphorate." By J. WALKER, D.Sc.

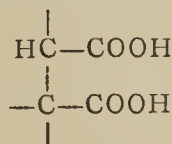
By electrolysing sodic ethylic camphorate, prepared by the direct union of camphoric anhydride and sodium ethoxide, the author has obtained the ethylic salts of two new acids, C₈H₁₃·COOH and C₁₆H₂₈(COOH)₂, which he proposes to term *campholytic acid* and *camphothetic acid* respectively.

Camphothetic acid is a colourless crystalline solid melting at 132°. It behaves as a saturated bibasic acid, forming well-characterised crystalline salts.

Campholytic acid is a monobasic unsaturated acid. It boils at 240–242°, and is levorotatory. Its ethylic salt boils at 212°, and is dextrorotatory. Both readily take up bromine in the cold, forming dibromides. The dibromo-acid, C₈H₁₃Br₂·COOH, is a white crystalline solid which melts at 110°. Its alkaline salts at once decompose in aqueous solution according to the equation C₈H₁₃Br₂·COONa = C₈H₁₃Br + CO₂ + NaBr, the compound C₈H₁₃Br being unsaturated, readily uniting with bromine in the cold.

It is pointed out that from the nature of the electrolysis

and the above-mentioned decomposition of the dibromo-acid, camphoric acid itself must contain the group—



DISCUSSION.

Dr. COLLIE having pointed out that the method by which Dr. Walker had obtained campholytic acid was such that there was little probability any fundamental change occurred in the camphoric molecule during the process, Dr. ARMSTRONG said that electrolytic oxygen was probably by no means a mild agent, and he thought that in the present instance, as well as in the cases studied by Crum Brown and Walker, it was not improbable that the change was brought about by oxidation: the formation of unsaturated acids especially favoured this view, as these might be regarded as resulting from the displacement of carboxyl by hydroxyl and the subsequent separation of water, or an analogous set of changes. Dr. Walker's ingenious application of Fittig's conclusions was open to question, on the ground that we knew very little at present of the behaviour of closed chain bromo-acids; moreover, the fact that camphoric acid did not yield a fluorescein appeared to preclude the idea that camphoric acid was an acid of the succinic type. He was of opinion that, on the whole, the evidence was in favour of the view that camphoric acid was an acid of the glutaric type, and that Dr. Walker's acid was probably a tetrahydrometaxylene derivative containing the carboxyl in one of the methyls.

Dr. WALKER, in reply to Dr. Armstrong, stated that he did not consider it probable that the formation of either the synthetic or unsaturated ethereal salts during the electrolysis was due to oxidation at the anode. Murray had shown in the case of the electrolysis of potassium acetate that there was no sort of proportionality between complete oxidation to carbonic anhydride and "partial oxidation" to ethane, as might be expected if the formation of ethane was due to oxidation. The conditions of the electrolysis found most favourable for the production of synthetic products were such as would almost ensure complete oxidation of the dissolved substance if the primary action was the decomposition of water into oxygen and hydrogen.

*118. "The Hydrates of Hydrogen Chloride." By S. U. PICKERING.

The determinations of the densities of solutions of hydrogen chloride made by Kolb, and also some made by the author, show a strongly marked break indicative of the presence of a trihydrate. They are represented by an appreciably straight line from 0 per cent up to the composition of that hydrate (40 per cent), after which the deviation from straightness is very considerable. On performing a series of freezing point determinations the trihydrate was obtained in large transparent crystals melting at -24.9°; this melting point is lowered by the addition of excess either of water or of acid. This hydrate and the dihydrate, already isolated by Pierre and Puchot, are the only crystalline hydrates which were obtained.

The densities indicate the existence of a change of curvature of a very minor character at a point corresponding to the composition of a hexhydrate, and similar indications are noticeable both in Berthelot's and Thomsen's heat of dissolution determinations. The author's freezing point determinations can afford no evidence for or against such a hydrate, on account of there being a change in the crystallising substance at the point in question, but they indicate the existence of a decahydrate. Roscoe and Dittmar's determinations of the influence of pressure on the composition of the boiling acid suggest the presence of an octohydrate. It seems, therefore, probable that these three hydrates exist in solu-

tion, and that they are comparatively stable, as solutions of acid of strengths between the hexhydrate and the decahydrate may be distilled with very little change in spite of great variations in pressure, and are altered in composition to a very small extent by the passage of a current of air through them at temperatures between 0° and 100° .

119. "*A New Base from Corydalis Cava.*" By JAMES A. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER.

The authors describe under the name of *corytuberine* a new alkaloid which they have obtained by exhausting crude corydaline with hot water; it crystallises from a hot aqueous or alcoholic solution in beautiful silky needles, soluble in cold solutions of sodium hydrate and ammonia, moderately soluble in benzene, and nearly insoluble in ether and chloroform. When heated it begins to blacken about 200° , and then slowly decomposes without melting. Its aqueous and alcoholic solutions are slightly dextrorotatory. Analyses lead to the formula $C_{19}H_{25}NO_4$. The *chlorhydride*, $C_{19}H_{25}NO_4 \cdot HCl$, is obtained in small, well-formed, rhombohedral crystals when a solution of the base in chlorhydric acid is evaporated to dryness. The *sulphate*, $(C_{19}H_{25}NO_4)_2 \cdot H_2SO_4$, is obtained by the interaction of the chlorhydride and the calculated quantity of silver sulphate. The *platinichloride*, $(C_{19}H_{25}NO_4)_2 \cdot H_2PtCl_6$, is precipitated in the form of a pale yellow crystalline powder, slightly soluble in water, on adding hydrogen platinichloride to a solution of the chlorhydride in water. *Corytuberine* is only soluble to a slight extent in methyl iodide, but the *methiodide*, $C_{19}H_{25}NO_4 \cdot CH_3I$, can be prepared by digesting an alcoholic solution of the alkaloid with methyl iodide during several hours.

When treated with concentrated solution of hydrogen iodide, one molecular weight of *corytuberine* gives two molecular proportions of methyl iodide, showing that only two of the oxygen atoms are present as methoxy-groups; *corydaline*, on the other hand, has all its four oxygen atoms in this form of combination.

The authors also give some notes on yet another alkaloid which they consider to be distinct, not only from *corydaline* and *corytuberine*, but from all the bases of *Corydalis cava* hitherto described.

Extra Meeting, February 20th, 1893.

The Right Hon. Lord PLAYFAIR, K.C.B., LL.D., F.R.S.,
Vice-President, in the Chair.

Kopp Memorial Lecture.

120. "*The Life Work of Hermann Kopp.*" By T. E. THORPE, D.Sc., F.R.S.

Kopp was barely 32 years of age when, so far back as 1849, he was elected a Foreign Member of the Society. Born October 30, 1817, at Hanau, at 18 he proceeded to Heidelberg, where he studied chemistry under Leopold Gmelin. He graduated at Marburg in 1838, the thesis which he presented being on "A Method of Pre-determining the Density of the Oxides," a proof that he had already, when barely 21 years of age, been attracted by the problems which were to constitute the chief experimental labours of his life. From Marburg he went to Giessen, where, at Liebig's instigation, he studied the mode of decomposition of mercaptan by nitric acid, practically the only investigation in pure chemistry that Kopp ever published.

In 1841 he became Privat-Dozent at Giessen, and was appointed Extraordinary Professor in 1843. In 1852, on Liebig's removal to Munich, Kopp and Will were together made Ordinary Professors, but after a year he resigned the whole control to his friend and colleague, continuing, however, to work in the laboratory. He remained at Giessen nearly five-and-twenty years, and all his most important experimental work was done there. In 1863 he accepted a call to Heidelberg, and repeated attempts

to induce him to accept a position elsewhere were unavailing; "even Bunsen alone," he was wont to say, "keeps me fast in Heidelberg."

Kopp is best known to the literary world by his "*History of Chemistry*," the first volume of which appeared in 1843, and the fourth and last in 1847. Hofmann, his life-long friend, has told us that by the publication of this classical work, Kopp—then barely 30 years old—suddenly found himself famous. Much of the later historical matter he published grew out of materials collected for the preparation of an enlarged and improved edition of the great work, which Kopp postponed year after year in the hope of being able to make a further study of certain special periods.

On the death of Berzelius, in 1848, the leaders of the Giessen School determined to carry on the work which had mainly occupied the closing years of his life, and established *Liebig and Kopp's Jahresbericht*, which Kopp continued to edit until 1862. In 1851 he joined Liebig and Wöhler in the production of the *Annalen der Chemie und Pharmacie*, and his name appears on the title page of no fewer than 190 volumes of this famous periodical. He also found time to write his "*Introduction to Crystallography*," the section on Theoretical Chemistry in Graham Otto's *Lehrbuch*, and not a few minor essays.

As an investigator, he occupies an almost unique position, the one consistent purpose of his work having been to establish a connection between the physical and chemical nature of substances—to prove, in fact, that all physical constants are to be regarded as functions of the chemical nature of molecules. When he began his enquiries very few boiling-points were known even approximately; the thermal expansions of barely half-a-dozen liquids had been measured, and the very methods of making such measurements with precision had to be worked out. In fact, at the outset of his investigation, he found the physical constants with which he was more immediately concerned very much as Berzelius found Dalton's values of the relative weights of the atoms.

His more important memoirs naturally fall into comparatively few groups, viz., (1) those concerning the relations between the relative densities of substances and their molecular weights; (2) those treating of the relations between boiling-points and chemical composition; and (3) those relating to the specific heats of solids and liquids.

In nothing was his originality and ingenuity more strikingly manifest than in the construction of his apparatus; to a great extent he was his own instrument maker, and his materials were for the most part glass and cork; but no Japanese worker with his few and primitive tools ever produced results which in point of delicacy, finish, and accuracy surpassed those which Kopp obtained by means of his simple contrivances.

In discussing Kopp's various investigations, Professor Thorpe first considers his work on specific heats and its bearings.

His observations on the relation of boiling-point to composition are next discussed, and the various later observations of other enquirers are taken into account.

Kopp's researches on specific volumes form the last section of the lecture, this subject being dealt with in a very comprehensive manner, not only Kopp's work, but also that of subsequent observers, being fully taken into account, the historical development of the subject being explained and abundantly illustrated.

It is pointed out that by the examination of the very large quantity of experimental material which is now before us, we are driven to the conclusion that molecular volume is not a purely additive property. There is no longer room for doubt that the molecular volumes of substances are affected by far more conditions than we have hitherto taken cognizance of. The value $CH_2 = 22$ has no other significance than as expressing the average increment in volume in successive members of an homologous series: it is doubtful whether even this mean

value is correct; later observations appear to show that the value augments as the series is ascended. The relation $C=2H$ no longer applies to carbon compounds in general. What is true of carbon and hydrogen is equally true of oxygen, whether as carbonyl or as hydroxyl oxygen: no definite or uniform values can be assigned to oxygen such that the molecular volume of a liquid can be *a priori* determined. The values given by Kopp are simply mean values, but the actual volumes are affected by conditions of which as yet we have no very precise knowledge or any certain means of measuring. The values for other elements are affected by the same considerations: that of chlorine, for example, as it is obtained on the assumption that the values for carbon and hydrogen are constant.

At the conclusion of this section reference is made to Kopp's critical memoir on the subject, published in *Liebig's Annalen* shortly before his death, discussing the outcome of the various researches which followed his own: we rise from its perusal, says the lecturer, with the conviction that after all the work summarised takes us but little beyond the threshold of the fundamental truth of which Kopp was the first to perceive the indication.

Lord PLAYFAIR, in the course of his remarks at the conclusion of the lecture, mentioned the fact that he had known Kopp fifty-two years ago—they were pupils together under Liebig. He was with him when he was making his first specific volume determinations, and Kopp daily came to him to discuss the results. In the historical survey given by the lecturer there seemed to be one name missing, that of Dalton; it was by reading a memoir by Dalton on specific volumes of solutions—a memoir which was rejected by the Royal Society and published privately—that he had been led to pay attention to the subject: this memoir was full of suggestion.

Dr. GLADSTONE had known Kopp as far back as 1847 to 1848, when he worked in Liebig's laboratory. Kopp's individuality undoubtedly in those days exercised a strong influence over the students.

Professor RÜCKER spoke of the publication of memoirs describing the life work of men like Kopp and discussing its bearings and development as a very happy idea on the part of the Society and as likely to be of great value to scientific workers.

Hofmann Memorial Lecture.

An extra meeting of the Society will be held on Friday, May 5th, 1893, the anniversary of the death of A. W. von Hofmann, when addresses will be delivered by the Right Hon. Lord Playfair, K.C.B., F.R.S., V.P.C.S.; Sir F. A. Abel, C.B., F.R.S., V.P.C.S.; Dr. W. H. Perkin, F.R.S., V.P.C.S.

PHYSICAL SOCIETY.

Ordinary Meeting, March 10th, 1893.

Prof. A. W. RÜCKER, F.R.S., President, in the Chair.

Mr. W. WILLIAMS was elected a member of the Society.

Dr. C. V. BURTON read a paper "*On the Applicability of Lagrange's Equations of Motion to a General Class of Problems, with special reference to the Motion of a Perforated Solid in a Liquid.*"

The paper shows that to apply Lagrange's equations it is not always necessary that the configuration of the system should be completely determined by the co-ordinates, but that under certain conditions one need not consider whether the whole configuration is determined by the nature of the known co-ordinates, nor enquire what is the nature of the ignored co-ordinates. The result, which is arrived at by the aid of the "principle of least action" and the investigation given in Thomson and Tait's "*Natural Philosophy*" (2nd Ed., Part I., Sec. 327), is expressed by the following proportion. If the kinetic

energy of a material system can be expressed as a homogeneous quadratic function of certain generalised velocities, ψ, ϕ, \dots only, the coefficients being functions of ψ, ϕ, \dots only, and if this remains always true so long as the only forces and impulses acting are of types corresponding to ψ, ϕ, \dots , the equations of motion for the co-ordinates ψ, ϕ, \dots may be written down from this expression for the energy in accordance with the Lagrangian rule.

The author then applies the proposition to the case of a perforated solid with liquid irrotationally circulating through the apertures, and shows how it may be extended to any number of perforated solids. The results are not put forward as new, but the method of proof is believed to be different from anything given before. Mr. Bryan had recently given a direct hydrodynamical proof, but the author thought it desirable that the problem should be rigorously treated by the method of generalised co-ordinates, avoiding any assumptions as to the impulse of the cyclic motion, and proceeding entirely from the principles established by Lagrange and extended by Hamilton, Routh, and Hayward. Incidentally it is mentioned that in equations (10)^v and (10)^{vi} (Thomson and Tait, Part I., Section 327), the sign $\delta v / \delta \psi$ should be reserved. A difficulty which arises in applying the result of Section 319, Example G, in the same work to the motion of solids through liquids is also referred to.

A Criticism by Mr. A. B. BASSET on Mr. Bryan's recent paper, and also on Dr. Burton's paper, was read by Mr. ELDER.

Mr. Bassett regards the process employed by Mr. Bryan in obtaining the equations of motion as a distinctly retrograde step, and thinks the most scientific way of dealing with dynamical problems is to avoid the unnecessary introduction of any unknown reactions. The advantages of the theory of the impulse are described by Mr. Basset, and the parts which require care when applying the theory to cyclic irrotational motion pointed out. Comparisons are then made as regards simplicity, between the different methods of treating the subject which have been used by Mr. Bryan, Prof. Lamb, and himself.

With reference to Dr. Burton's paper, he thinks it will tend to complicate rather than elucidate the subject.

An account of how Lagrange's original equations had been modified by Hamilton, Routh, and himself is given at some length, and the advantages and power of the mixed transformation which he had developed are pointed out.

Prof. HENRICI said he agreed with Mr. Basset in preferring the more general method, but thought the independent treatment of optical problems, as given by Mr. Bryan and Dr. Burton, very desirable.

Dr. BURTON, in reply, said he concurred with Mr. Basset on some points, but thought it decidedly advantageous to look at problems from different points of view. The investigation he (Dr. Burton) had given was applicable to any number of solids, and, on the whole, simpler than Mr. Basset's.

The PRESIDENT pointed out that no attack had been made on the validity or accuracy of Mr. Bryant's or Dr. Burton's work. As to simplicity of the various methods, different opinions might be expected to exist. He himself thought it very desirable that such problems should be approached from different sides.

Prof. G. M. MINCHIN read a paper on "*The Magnetic Field of a Circular Current.*"

Since the magnetic force at any point is the curl of the vector potential at that point, the latter quantity had been calculated for any point P in space. Taking the axis of the circle as the axis of z , the line through the centre of the circle and the foot of the perpendicular from P on the plane of the circle as the axis of x , and the line perpendicular to x and z as that of y , it was shown that the only component of the vector potential is G, parallel

to y , and that $G\alpha$ is constant along a line of force, α being the x co-ordinate of P . The expression for $G\alpha$ is—

$$G\alpha = i\rho \{2(K-E) - k^2k\},$$

where i =strength of current, ρ and ρ' the distances of P from the furthest and nearest points of the circle, $k^2 = 1 - \frac{\rho'^2}{\rho^2}$, and K and E complete elliptic integrals of the first and second kinds with modulus k . The quantity in brackets being a function of $\frac{\rho'}{\rho}$ only, $G\alpha$ may be written in the form $i\rho f\left(\frac{\rho'}{\rho}\right)$, which shows that at all points for

which ρ'/ρ is constant, $G\alpha$ varies directly as ρ . Since the lines of force in all planes passing through the axis of the circle are the same, attention need only be paid to that containing the point P . The locus of points for which ρ'/ρ is constant is then a circle, whose diameter is the line joining the points which divide the diameter of the circle in which the current flows, internally and externally in the given ratio, and this circle cuts the one described on the diameter of the current circle, orthogonally. A series of such circles corresponding to different values of ρ'/ρ are then drawn, and the values of $2(K-E) - k^2K$ calculated for each by aid of a table of Elliptic Integrals. Denoting these quantities by Q' then $G\alpha = i\rho Q'$; hence $i\rho Q'$ is constant along a line of force. If P be taken on one of the circles for which the value Q' is Q'_0 , then the point P_1 at which the line of force through P cuts the circle whose constant is Q'_1 , can be found from the equation $\rho_1 Q'_1 = \rho_0 Q'_0$, for since ρ_0 , Q'_0 , and Q'_1 are known, ρ_1 is easily determined, and the position of P_1 plotted. The circles above described also serve for drawing the lines of equal vector potential, and through a mistake in calculation the method of drawing the lines explained in the printed proof of the paper is one which gives the vector potential lines instead of the lines of force.

The author points out that the fundamental definition of vector potential is unsatisfactory, for it leads to the result that the vector potential is infinite at every point in the field of a long straight current. A way of avoiding the difficulty by only considering *differences* of vector potential is described. In the latter part of the paper a complete expression for the conical angle subtended by a given circle at any point in space is worked out, and the result given in terms of two complete elliptic integrals of the third kind, the parameter and modulus of one being $\frac{2\nu}{2-\nu}$, and k , respectively, and those of the other $\frac{-2\nu}{1+\nu}$, and k . The value is—

$$2\pi - \frac{z}{\rho r} \left\{ \frac{r+a}{1-\nu} \Pi\left(\frac{2\nu}{1-\nu}, k\right) + \frac{r-a}{1+\nu} \Pi\left(\frac{2-\nu}{1+\nu}, k\right) \right\}$$

where ρ and k have the same meanings as before, z is the z co-ordinate of P , a the radius of the circle, r the distance from P to the centre of the circle, ν the size of the angle between the radius vector r and the axis of the circle, and $\Pi\left(\frac{2\nu}{1-\nu}, k\right)$ elliptic integrals of the third kind.

Prof. PERRY thought the problem had been very prettily worked out, and hoped Prof. Minchin would be able to extend the solution to cylindrical coils,—a subject in which he (Prof. Perry) had long been interested.

Mr. BLAKESLEY read a note by Mr. Niven pointing out that the locus of points for which the ratio ρ'/ρ is constant was an anchor ring.

Prof. MINCHIN maintained that the locus was a sphere, and on this subject a short discussion arose, in which the PRESIDENT, Prof. PERRY, Prof. MINCHIN, Dr. BURTON, and Prof. S. P. THOMPSON took part.

Dr. SUMPNER described a method of drawing the lines of force of a circular current, or of any circuit, symmetrical about an axis, by a purely experimental and

graphical process. The strengths of field were first determined at several points in the plane of the current, and from these results the points through which lines of force were to pass in order that their distribution might indicate the strength of the field at all points were graphically deduced.

A paper on "*The Differential Equation of Electric Flow*," by Mr. T. H. BLAKESLEY, was postponed.

CORRESPONDENCE.

SEPARATION OF WOOL AND COTTON.

To the Editor of the Chemical News.

SIR,—Cotton and wool may be separated from each other by operating on two samples of the textile material, using a solution of caustic soda in one case and dilute sulphuric acid in the other case. On boiling, the wool will be removed in the first case, whilst the cotton will be left; in the second case, the cotton will be removed, whilst the wool will be left. The fibres are then in a condition fit for further examination if required.

If a sample be heated for some time to 280° F., the wool can be rubbed out as dust, whilst the cotton will only be rendered slightly tender. Of course, in this case the character of the wool as regards staple, &c., will be lost.

If a sample be dipped into dilute sulphuric acid and hung up for some time in a warm place, the cotton will be destroyed; on washing and drying, the weight of wool is obtained. The loss is due to cotton, size, starch, mineral matter, &c.

Undyed mixtures may be boiled in a weak solution, say, of eosine; wool takes a faint pink colour, the cotton is unaltered. Dyed mixtures may in most cases be recognised by the action of dilute acids; especially if dyed in the piece, and in many cases if dyed in the hand.—I am, &c.,

THOS. T. P. BRUCE WARREN.

NOMENCLATURE OF MILK ALBUMENOIDS.

To the Editor of the Chemical News.

SIR,—Dr. Halliburton has proposed to give the name "caseinogen" to that albumenoid of milk hitherto known as casein, and to reserve the name casein for the curd produced by the action of rennet on "caseinogen." There are very serious objections to this nomenclature; it is inadmissible, etymologically, to combine the Latin word casein with the Greek root gen. Moreover, the termination gen is not here used in its proper pristine sense. In the words hydrogen and chromogen, for instance, it signifies that these compounds form integral parts of water and colour respectively, and not that a certain decomposition product can be obtained from them. In the word "caseinogen," and its kinsman "fibrinogen," a totally different meaning is given to the termination. Nowadays, it is true, that the etymology of a word matters little, and were there not other objections to the use of the word, it might pass. The name "casein" for the parent compound has the claim of priority, one might almost say of antiquity, while the reservation of the name for a secondary product, which has small chemical claims to be placed in the class of albumenoids to which the termination "in" belongs, is unjustifiable.

As the name "caseinogen" has not been adopted, except by the school of which Dr. Halliburton is the worthy head, may I appeal through your columns to him and his associates to re-consider the question of nomenclature? If I may be permitted, I would suggest the name

"chymo-dys-caseose" for the curd produced by rennet; "chymo" expresses that it is produced by rennet, and "dys" shows its analogy to the so-called casein-dyspeptone.

I would further suggest the following system of naming the derivatives of casein:—Those produced by rennet, chymo-dys-caseose and chymo-proto-caseose; those produced by pepsin, pepto-proto-caseose, &c., and pepto-caseone; and those produced by the pancreatic ferment, trypto-proto-caseose, &c.; for the caseose produced by the action of acids, hydrolo-caseose might be adopted. I put forward these suggestions for consideration; the system, which is expressed in the words themselves, might be extended to other albumenoids.—I am, &c.,

H. DROOP RICHMOND.

50, Clanricarde Gardens, Bayswater,
March 13, 1893.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 9, February 27, 1893.

Physical Properties of Melted Ruthenium.—A. Joly.—This memoir will be inserted in full.

Determinations of the Atomic Weight of Lead by Stas.—G. Hinrichs.—The author asserts that Stas has not succeeded in determining the atomic weight of lead, and considers that if he had operated upon 15–25 grms. of lead he would have obtained higher results.

Aldehyds of the Terpenes.—A. Etard.—The author describes camphenic aldehyd, $C_{10}H_{14}O$, and camphenic acid, $C_{10}H_{14}O_2$.

Constitution of the Hydrated Alkaline Phenates.—M. de Forcrand.—A thermo-chemical paper not susceptible of useful abstraction.

Alkaloids of Cod-Liver Oil, their Origin, and their Therapeutic Action.—J. Bouillot.—The author includes all the alkaloids of cod-liver oil under the joint name pangaduine. He concludes that they are not the result of any fermentation, but exist in the normal hepatic tissue.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. ix. and x., No. 1, January 5, 1893.

Trials of Different Methods of Preparing White Wines, and on the Composition of a Red Wine.—J. A. Müller.—The author concludes that if the wine obtained, by fermenting the mixture obtained on treading entire clusters under foot, is inferior to that from the fermentation of the juice, obtained by expressing the grapes, it is that the latter contains a smaller quantity of acids, of tannin, and of mineral salts than the former.

New Process for Detecting Foreign Substances and especially Colouring-Matters in Wines.—M. Marouby.—The author proposes a series of test papers cut into circular discs. On placing on one of the discs a drop of the suspected wine, the spot appears surrounded by a halo of different colours.

Journal für Praktische Chemie.
New Series, Vol. xlvi., Part 4.

Researches on Substitution in the Aliphatic Series.—Victor Meyer and Fr. Müller.—This lengthy memoir does not admit of useful abstraction.

Constitution of Sodium Acetacetic Ether.—Arthur Michael.—It has been already shown that the change of structure which occurs in acetacetic ether is by no means isolated among organic reactions, but that in such transpositions the true explanation of the phenomenon is to be sought, which has been called tautomerism, desmotropy, or pseudo-form, and also that reactions are often viewed as results of substitutions, whilst they are truly processes of addition. The explanation given by Laar contains a germ of truth, as it connects the phenomenon with a "motile," or, more accurately, with a reactive hydrogen. But by assuming the continuous movement of this hydrogen, Laar has drawn away attention from the true cause. On surveying the known cases of desmotropy it will be found that the question is not concerning a motile hydrogen, but that in the supply of such a hydrogen the equilibrium of the atoms may be disturbed, and a more stable arrangement may be effected. There are also cases where such a transposition of atoms may be effected by the combination of an acid with a basic substance. In this sense there exist altogether under the same conditions no desmotropic or tautomeric substances, but merely desmotropic or tautomeric derivatives of substances which, as soon as they obtain their former conditions by substitution or by removal of the basic or acid constituents, return to their old constitutions by atomic transposition. Certain theoretic conceptions have been already connected with tautomerism, desmotropism, and pseudo-form, and I may therefore be permitted to propose for this phenomenon the name merotropism.

MISCELLANEOUS.

Correction.—We find to our regret that the article by Prof. Hampe on "The Simultaneous Precipitation of Copper and Antimony by the Electric Current," which appeared in the *CHEMICAL NEWS*, vol. lxvii., p. 103, has, by an oversight, not been credited to the *Chemiker Zeitung*, in which it originally appeared. It is of course our duty to acknowledge this error.

Researches on Alloisomerism.—Arthur Michael.—These researches consist of memoirs on the addition of bromine to acetylendicarbonic acid and its ethyl ethers, by A. Michael; on the action of sodium ethylate upon dibromsuccinic ether, by A. Michael and C. C. Maisch; on the crotonic acids and their derivatives, by A. Michael and O. Schulthess; on the formation of solid crotonic acid in the reduction of allo- α -brom- and chlorcrotonic acid, by A. Michael; on the addition of bromine and chlorine to solid crotonic acid, by H. Abbott Michael; and contributions to a knowledge of some homologues of malic acid, by A. Michael and G. Tissot.—*Jour. Prakt. Chemie*, New Series, xlv., Parts 5–7.

The Chemical Laboratory of Wiesbaden.—According to the *Chemiker Zeitung* the Chemical Laboratory of Geh. Hofrath Prof. Dr. R. Fresenius has, during the winter term, been attended by sixty-one students. Of these forty-five are from Germany, five from North America, three from Austria, three from Russia, one from England, one from Holland, one from Belgium, one from Spain, and one from Java. There were three assistants in the tutorial laboratory, four in the Versuchsstation, and seventeen in the various departments of the laboratory of research. The staff, including in addition to the Principal, Profs. H. Fresenius and Borgmann, Drs. W. Fresenius, E. Hintz, Frank, and the architect Brahm, will be augmented by Dr. W. Lenz, lecturer for microscopy. The next term begins on April 24. In addition to scientific work (purely) there have been conducted, during the winter, numerous investigations in the interest of commerce, the arts, mining, agriculture, public health, and justice.

The Permeability of the Skin for Microbia.—B. Wasmuth.—The researches which the author has conducted upon himself with *Staphylococcus pyogenes albus* and *aureus*, with *Staphylococci*, and the cocci of erysipelas upon rabbits, guinea-pigs, and white mice, and with virulent splenic fever on guinea-pigs, prove that the healthy, uninjured skin of man and other animals is permeable for micro-organisms. They find entrance along the sheath of the hairs, but not by the sudatory pores. Inunction with microbia mixed with lanoline makes no difference in the nature and the speed of the infection.—*Centralblatt für Bakteriologie und Chemiker Zeitung*.

The Part Played by Flies in the Dissemination of Cholera.—J. Sawtschenko.—Whilst we already know from the researches of Celli (*Centralblatt f. Bakteriologie*, 1888, iv., 486), that the bacteria of tubercle, splenic fever, abdominal typhus, and European cholera pass unhurt through the digestive organs of flies, and reappear in their excrements without having forfeited their virulence, similar observations had until the present not been made with the bacteria of Asiatic cholera. The author's researches in this direction have supplied the deficiency and led to the following results:—In the intestines of flies which had been fed on cholera cultures, the bacteria of cholera were easily recognised after periods of twenty-four, forty-eight, seventy-two, and in one case ninety-six hours. In the contents of the intestines of flies, which had been fed not with pure cholera cultures but with excrements, or with the contents of the small intestine of patients who had died of cholera, Koch's cholera bacteria were still to be distinguished after twenty-four, forty-eight, and seventy-two hours along with other bacteria to be met with in the materia used for infection. The cholera bacteria obtained from the intestines of flies did not lose their virulence even after forty-eight to seventy-two hours. In view of these results the author takes up the question whether flies merely disseminate by their excreta the cholera bacteria which they have taken up, or whether the bacteria do not at suitable temperatures and under suitable dietetic conditions of nutriment multiply within the digestive system of the flies. He considers the latter case as the more probable. Hence in this case the flies would not be regarded merely as disseminators of infections, but, in part at least, as its foci from which new, fresh generations of cholera bacteria perpetually arrive upon our food.—*Centralblatt für Bakteriologie und Chemiker Zeitung*.

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Medical, 8.30.
— Society of Arts, 5. "Alloys," by Prof. W. Chandler Roberts-Austen, C.B., F.R.S. (Cantor Lectures).
- TUESDAY, 21st.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "Physical and Psychological Neurology," by Prof. Victor Horsley, F.R.S.
— Society of Arts, 8. "Newfoundland," by Cecil Fane.
— Pathological, 8.30.
- WEDNESDAY, 22nd.—Society of Arts, 8. "The Manufacture of Non-Poisonous White Lead," by Perry F. Nursey, C.E.
— Geological, 8.
- THURSDAY, 23rd.—Royal, 4.30.
— Royal Institution, 3. "The Great Revival—A Study in Mediaeval History," by the Rev. Augustus Jessopp, D.D.
— Institute of Electrical Engineers, 8.
— Chemical, 8. (Anniversary).
- FRIDAY, 24th.—Royal Institution, 9. "Interference Bands and their Applications," by Lord Rayleigh, F.R.S.
— Physical, 5. "On the Differential Equation of Electric Flow," by Thomas H. Blakesley, M.A. "Experiments on the Viscosity of Liquids," by Prof. Perry, J. Graham, and L. W. Heath.
- SATURDAY, 25th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

CHEMICAL LABORATORY, WIESBADEN, GERMANY.

Director—Prof. R. FRESENIUS, Ph.D.

Practical Instruction in the Laboratory Prof. R. FRESENIUS, Ph.D.
Prof. H. FRESENIUS, Ph.D.
W. FRESENIUS, Ph.D.
E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) Prof. H. FRESENIUS, Ph.D.
Experimental Physics W. FRESENIUS, Ph.D.
Stoichiometry E. HINTZ, Ph.D.
Organic Chemistry W. LENZ, Ph.D.
Chemical Technology
Microscopy, with exercises in Microscopic work
Chemistry and Analysis of Foods .. Prof. H. FRESENIUS, Ph.D.
Prof. E. BORGMANN, Ph.D.
W. FRESENIUS, Ph.D., and
E. HINTZ, Ph.D.
Hygiene Dr. med. G. FRANK.
Practical exercises in Bacteriology ..
Technical Drawing, with exercises .. J. BRAHM.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to the undersigned.

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THE CHEMICAL NEWS.

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THE CHEMICAL CONSTITUTION OF THE ATMOSPHERE FROM REMOTE GEOLOGICAL PERIODS TO THE PRESENT TIME.

By Dr. T. L. PHIPSON, F.C.S.,
Formerly of the University of Brussels,
Member of the Chemical Society of Paris, &c.

THE chemical constitution of the atmosphere must have varied in successive ages just as the various flora and fauna of the earth have changed. The presence of combustible substances such as pyrites, molybdenite, copper pyrites, and graphite, in the primitive rocks, long ago appeared to me to point clearly to the fact that if these rocks had been formed by fusion and crystallisation by slow cooling, free oxygen must have been absent from the air.* Again, that carbonic acid must have been present in the atmosphere in much larger quantities than at present during the period of the coal-flora has appeared to many to be proved by the enormous residues of carbon, as compared with the more recent deposits of lignite and peat.

Water and air are considered by most modern authors as the *residues* left after the cooling of the earth—residues of stupendous chemical action, the formation of which residues rendered the globe fit for the existence of organised beings. But was the air in these primitive periods such as we now know it?

In a former paper† I promised to examine the doctrine set forth on this interesting subject by the late Prof. C. J. Koene, of the University of Brussels, in a series of popular lectures to which I have already referred. In order to place this theory on as fair a footing as possible, I shall add some considerations on the respiration of the lower forms of animal life, and will quote Ch. Martins's opinion regarding the compensation theory of Dumas; also Hoeser's reason why plants must have appeared before animals, and Reiset's recent analytical results for carbonic acid in the air of the open country, &c.

I do not wish it to be understood that I endorse Koene's theory as a whole, for it appears to me beyond the realms of even the most advanced science to solve questions of this nature, though he did not think so.

Four great names appear in connection with this subject, Jean Baptiste Dumas and Justus Liebig on the one hand, Berzelius and Mulder on the other. The two former appear to have considered the chemical composition of the atmosphere to be permanently fixed for an indefinite period (and perhaps they admitted it always to have been so since the first appearance of life upon the globe), basing their views upon the fact that whilst plants give out oxygen and absorb carbonic acid, animals absorb oxygen and reject carbonic acid. Dumas and Liebig looked upon the animal and vegetable kingdoms as indispensable one to the other, and believed that their mutual action upon the atmosphere would keep its composition constant. Ch. Martins, a celebrated French naturalist and contemporary of Dumas, criticised this compensation theory by pointing out the extremely minute quantity of air affected by the respiration of plants and animals as compared with the vast bulk of oxygen in the atmosphere. Thus he shows that the atmosphere containing 134,000 cubic measures of oxygen, the entire animal world only con-

sumes in a century 15 to 16 of these cubic measures (this is Dumas's own calculation); hence, says Prof. Ch. Martins, "the constant composition of the air, one of the elements of which, oxygen, is constantly transformed into carbonic acid by men and animals, does not depend upon a *pretended equilibrium between the respiration of plants and animals*, but upon the fact that the quantity of oxygen consumed by animals is out of all proportion to that contained in the entire atmosphere" (*Météorologie et Physique du Globe*).

Berzelius felt convinced that oxygen must gradually diminish in quantity in the air, for he declared he knew of *no de-oxidising process sufficiently great and general to set at liberty all the oxygen which combined, every instant, with combustible material* (*Traité de Chimie*).

The great Dutch chemist Mulder goes still further; he insists upon the enormous production of carbonic acid by the respiration of animals, fermentation, volcanic action, and human industry, and notes the constantly increasing destruction of forests, those vast manufactories of oxygen gas. He concludes that *carbonic acid must increase, and that oxygen has continued to decrease since the first appearance of life upon the earth*. With regard to volcanic action I myself have calculated roughly, on the spot, the quantity of carbonic acid produced by a small chalybeate spring near Neubau in the principality of Waldeck (Germany) in the year 1865. It was a little over one pound per hour, or *about a quarter of a cwt. per diem*; and this is only one of thousands of similar springs scattered over the surface of the globe.

Koene upholds a contrary theory, according to which the *carbonic acid and nitrogen of the air have never ceased diminishing since the origin of living creatures, whilst the relative proportion of oxygen has gone on increasing*.

In the more remote geological ages there could have been no free oxygen at the high temperatures to which all combustible bodies were exposed, and we can only conceive the atmosphere, when the earth had cooled sufficiently, to have been composed of nitrogen, carbonic acid, and vapour of water. Such is the starting-point of Koene's doctrine. He admits that when circumstances permitted the existence of living beings, plants (or *protocista*, let us say, which cannot be classed either as plants or animals)* first appeared and prepared, during a vast lapse of time, the surface of the earth for the existence of higher organisms. These first beings, according to Koene, were *anaerobic*: that is, they were capable of existing without free oxygen. It is interesting to note that some fifteen years after this theory was first professed, Pasteur actually discovered anaerobic microbes.

It would be easy to admit, with the school of Lamarck and Geoffroy St. Hilaire, that, as circumstances changed, these anaerobic *protocista* gave rise to *aërobic* beings and plants. Anyhow, to return to Koene's theory, *plants were the first producers of oxygen*, and they produced it in constantly increasing quantities as ages rolled by, until it appears to have attained its greatest proportion during the coal-flora period; the enormous leaves of these plants fed luxuriously on the rich carbonic air, and set free immense quantities of oxygen.

Hoeser's opinion that plants first appeared is exposed in the few lines: "Starting from the theoretical view of the gradation of organised beings, and looking upon *vegetable life as a necessary condition of animal life*, the former must, consequently, have appeared before the latter." Alex. von Humboldt made a very weak attempt to disprove this by alluding to the fact that the Eskimo live almost exclusively on fish and cetacea.

It is quite possible that plants of those remote geological periods might have flourished in an atmosphere so rich in carbonic acid that it would kill plants of our modern period. I have only made very few experiments on this subject, but I hope to make more. In those I have made with such plants as the lilac, the willow, &c.,

* Some modern writers have supposed that granite has never been heated beyond 500° C., but we find a higher temperature than that in a modern lava when it is comparatively cool.

† "Koene and Stas: Chemistry at Brussels, 1840—1860" (CHEM. NEWS, vol. lxvii. p. 51).

* Phipson, "Protocista, &c." (*Jour. de Médecine*, Brussels, 1861).

I have found that an excess of carbonic acid destroys them, and I cannot yet say whether our modern flora possesses any plants which would thrive in an atmosphere overcharged with carbonic acid.

The next point to which the theory refers is that an immense quantity of carbon is fixed in the earth by the remains of plants and animals, and never returns to the air; at the same time nitrogen is also fixed in like manner, and is extracted daily from the air in vast amounts to form ammonia and nitrates. Oxygen alone remains in relatively larger and larger proportions; it has increased since the first living beings appeared, and, curious to relate, *its maximum corresponds with the maximum development of the central nervous and brain tissue*. As for carbonic acid, it has almost entirely gone. For the last half-century it has been noted as only six, five, and four parts on 10,000 parts of air. The latest determinations by Reiset (a most careful chemist, pupil of Boussingault, and one of the editors of Millon's well-known "Annuaire"), made in the open air at a country place many miles from Paris, gave three parts on 10,000 parts in 1889, and he could not get a fraction more.

One of the most expert chemists of modern times, Pelouze, says on this subject: "On comparing the analyses of atmospheric air undertaken some years ago by Gay-Lussac with those made quite recently [Pelouze wrote in 1848], we recognise that the proportion of oxygen and nitrogen have not varied in that interval. However, as the methods of analysis, though greatly improved, are not absolutely exact, it is quite possible that the composition of the atmosphere is undergoing very slight variations which will only become appreciable after a great number of years" (*Abrégé de Chimie*).

Baudrimont about the same time wrote: "The atmosphere is eminently variable, and whatever means of reparation Nature may employ, it is more than probable that it will change to such a degree as no longer to support life" (*Traité de Chimie*, vol. i.).

Anatomists cannot tell us how respiration is effected in the lowest creatures in the scale of life,—those which are supposed to have been the first produced. They simply say all vestiges of respiratory organs are absent, unless it be the cell wall or outer envelope. They do not say whether these beings require free oxygen or not, though this can be proved for the higher organisms, such as fish and tadpoles, which live in water, and I have found that the minute *Protococcus palustris* carries on its respiratory functions much as the higher organised plants do.* In such animals as *Holothuria tubulosa*, the function of respiration is little, if at all, separated from that of the intestine. Water is sucked in three times a minute, and remains about twenty seconds in the animal's body. It is not yet known whether the lower forms of life may be able to derive oxygen from water or carbonic acid, or both; but it appears evident that oxygen is essential for plants and animals however low in the scale; in fact, oxygen and life seem to be synonymous terms in this respect.

To return once more to Koene's doctrine, it is based, as I have shown, upon the *incomplete eremacausis* of organic matter confided to the earth and protected from the action of the air, by which enormous quantities of carbon and nitrogen have always been and are still slowly being subtracted from the atmosphere. He does not believe that either of these elements can be supplied from without—from cosmic space—and they disappear thus for ever from the air.

Against this view it may be asked, Is this eremacausis or slow combustion incomplete? Is not carbonic acid returning in immense quantities to the atmosphere, not only by the respiration of animals and volcanic action, but by the agency of man himself? In time, the whole of those vast deposits of coal and lignite formerly taken from the air will return as carbonic acid; and if forests

continue to be constantly annihilated, as Mulder remarked, to make room for clay and stone buildings, will not carbonic acid increase until it predominates, as it is supposed to have done in primitive times?

Koene has alluded to the coincidence of the higher development of the central nervous system and brain power, with the present increased quantity of oxygen in the air. Man, he says, has become more and more excitable; he now lives faster, prefers intellectual to physical activity, desires shorter hours of labour [this was written in 1856], strives actively for recreation or enjoyment, and rarely, if ever, attains to the age of the patriarchs. Vitality, nervous power, and oxygen have increased together upon the earth from the earliest ages, and the history of this increase can be read by the chemist in the records of the earth's strata.

In conclusion I cannot avoid showing the weak points of this ingenious theory when considered from a purely philosophical aspect. Koene admits oxygen to be the product of life, whilst it is the condition of life, and finally, that its predominance will be the cause of universal death. This is certainly paradoxical; but, as I hinted before, the solution of these problems is probably beyond the powers of Science.

Putney, March, 1893.

A CURIOUS FORMATION OF THE ELEMENT SILICON.

By H. N. WARREN, Research Analyst.

DURING the preparation of specimens of crystalline and other forms of silicon, I obtained a most curious formation of that substance which would appear, when treated analytically, to be composed of graphitoidal silicon, constituted so as to form most perfect and well developed crystals consisting of oblique octahedrons. This peculiar modification of the element first made its appearance upon subjecting potassium silicofluoride to a most intense heat in contact with impure aluminium. Upon separating the graphitoidal silicon thus formed by the aid of dilute acids, small quantities of the other substance were observed. Direct steps were at once taken to procure it, if possible, in larger quantities, after numerous experiments had failed to reproduce it. The following method was used with success, although still very uncertain.

Graphitoidal silicon was first obtained by introducing pieces of metallic aluminium about the size of a walnut into a clay crucible of convenient dimension, and subjected to a heat sufficient to maintain in a fused state a mixture of four parts potassium silicofluoride, one of potassium chloride, and two of potassium carbonate. After the violent reaction attending the introduction of the aluminium had subsided, the crucible was urged to whiteness for about five minutes; after cooling and breaking the same, a perfect round button consisting of about 80 per cent silicon was obtained. This, after carefully detaching any adhering slag, was placed in a plumbago crucible in contact with about twelve times as much aluminium as the button originally obtained, together with an addition of two parts by weight of metallic tin, and covered with a layer of sodium silicate. The crucible with its contents were then subjected to the most powerful heat that could be obtained for about two hours. After cooling and breaking the piece of aluminium contained therein, the new modification was obtained in large perfect crystals possessing a full metallic lustre, and true models of oblique octahedrons.

After dissolving the small quantity of aluminium mechanically entangled, the analysis of the crystals denoted the existence of pure silicon only, being insoluble in all acids, except hydrofluoric acid, and infusible.

In appearance the crystals resemble crystals of cast iron, which are sometimes met with upon breaking a pig

* Phipson, "Production of Oxygen by *Protococcus Pluvialis*" *CHEMICAL NEWS*, 1883).

of that substance, the largest assuming a size of over half an inch across the faces, and as perfect as a crystal of alum; in fact, it would be difficult to say as to what dimension these crystals could be obtained, as the author has on more than one occasion obtained perfect models over an inch and a half in length and thickness.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

RAPID PREPARATION OF CHROME AND MANGANESE AT A HIGH TEMPERATURE.

By HENRI MOISSAN.

CHROME and manganese, for which we indicate in this paper a rapid method of preparation, are most commonly obtained in laboratories by reducing the oxide by means of carbon. Industry has utilised this reaction for producing in blast furnaces larger quantities of ferro-manganese and of ferro-chrome.

The use of the electric furnace enables us to convert these long and difficult reductions into ordinary lecture experiments.

The oxides of nickel and cobalt are also rapidly reduced by means of carbon in the electric furnace. Under these conditions we have obtained cast metals containing:—

	I.	II.	III.	IV.
Ni	85.00	85.82	90.60	94.06
C	14.59	13.98	10.20	6.35

A specimen of cobalt prepared with an excess of oxide gave us in three successive analyses:—

C per cent	0.726	0.732	0.741
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Manganese.—Pure manganese oxide is mixed with coke and ignited in the arc. On operating with 300 ampères and 60 volts the reduction is complete in five or six minutes. There remains at the bottom of the crucible a regulus of manganese carbide of from 100 to 120 grms.

The reduction is made rather more slowly, requiring from ten to fifteen minutes with a voltaic arc measuring 100 ampères and 50 volts.

On operating in presence of an excess of coke the manganese is saturated with carbon and we obtain cast metals yielding on analysis the following figures:—

	I.	II.	III.	IV.
Mn	85.00	85.82	90.60	94.06
C	14.59	13.98	10.20	6.35

But if the reduction is produced in presence of an excess of oxide, the quantity of carbon decreases much, and in certain ingots we do not find more than from 4 to 5 per cent of carbon. When the cast manganese thus prepared contains only little carbon, the metal may easily be preserved in open vessels; but as soon as the quantity of carbon increases, the moisture of the air quickly decomposes the carbide. Small fragments laid in water are transformed in twenty-four hours, yielding a gaseous mixture of hydrogen and hydrogen carbides.

Chrome.—We know that the reduction of chromium sesquioxide by carbon is much more difficult than that of manganese oxide. This operation in the electric furnace requires only from eight to ten minutes if we have at our disposal a current of 350 ampères and 50 volts.

The mixture of ignited chromium sesquioxide and of carbon is easily reduced and leaves a brilliant regulus, perfectly melted, of from 100 to about 110 grms. With a current of 50 volts and 100 ampères the experiment is made on a smaller quantity of substance in fifteen minutes as a maximum.

A current of 30 ampères and 50 volts suffices to yield a regulus of 10 grms. in thirty or forty minutes.

The melted metal adheres to the crucible. According

as the quantity of oxide or of carbon predominates, we obtain a metal richer or poorer in carbon. The different specimens obtained under these conditions gave the following figures as their percentage of carbon:—

	I.	II.	III.	IV.
Cr	87.37	86.25	90.30	91.70
C	11.92	12.85	9.47	8.60

If we obtain this cast chrome it may be refined by a second operation. The metallic carbide obtained as above, broken into coarse fragments, is placed in a coke crucible, carefully lined with chromium oxide, and covered with the same oxide. This mixture is submitted anew to the temperature of the electric arc; superficial oxide melts, then the metal enters into fusion and loses by degrees all the carbon which it contains. The chrome thus prepared being heated in a current of chlorine is converted into a volatile chloride without leaving a trace of carbon.

This process renders it possible to obtain metallic chrome rapidly and in a rather large quantity. It does not require a very important outlay if we have at disposal motor power produced by a fall of water, since the dynamo used in these experiments cost only 1200 francs.

This reduction is not effected only with chromium oxide produced in the laboratory; it may also be produced from chrome iron as met with in nature. We then obtained a melted and perfectly homogeneous alloy of iron and chrome. It is easy to convert the chrome of this alloy into a chromate. The alloy, coarsely powdered, is thrown into a melted bath of an alkaline nitrate; there are produced insoluble ferric oxide and alkaline chromate soluble in water and capable of being purified by re-crystallisation.

These experiments have been made at the Conservatoire des Arts et Métiers by the kind permission of Colonel Laussedat.—*Comptes Rendus*, cxvi., No. 8.

A VOLUMETRIC METHOD FOR THE DETERMINATION OF LEAD.*

By F. C. KNIGHT.

(Concluded from p. 129).

THE lead taken for the following experiments was dissolved in 5 c.c. concentrated nitric acid, 10 c.c. concentrated sulphuric acid added, and evaporated until the sulphuric acid fumes appeared. To the mass, when cool, water was added, and the sulphate of lead filtered off, washed first with hot water acidified with sulphuric acid, and finally with hot water alone. The sulphate of lead was then rinsed off the filter into a beaker, 3 c.c. concentrated hydrochloric acid added, and enough water to bring the bulk to about 100. The solution was boiled until the whole of the sulphate of lead was dissolved and 2 grms. of pure granulated zinc added. After an action of five minutes, an additional 0.50 gm. of zinc was introduced, and the solution again brought to the boiling point, when 10 c.c. more of concentrated hydrochloric acid were added. In a few minutes all of the zinc had dissolved. The solution was decanted from the lead sponge, the latter washed, re-dissolved in nitric acid, and the precipitation as oxalate made as before described. The results were:—

Exp. No.	Weight of lead taken. Grm.	KMnO ₄ used. C.c.	Weight of lead found.	Per cent obtained.
14.. ..	0.22150	42.9	0.22007	99.76
15.. ..	0.21134	40.9	0.20981	99.32
16.. ..	0.20756	40.2	0.20632	99.39
17.. ..	0.16683	32.5	0.16672	99.94

The average percentage obtained being 99.60.

* A Paper read before the Colorado Scientific Society, Nov. 7, 1892. From the *Journal of Analytical and Applied Chemistry*, vi., No. 11.

It has been mentioned that when pure sulphate of lead in hydrochloric acid solutions is precipitated with granulated zinc it comes down in a coherent spongy mass. This is, however, not the case when certain impurities are associated with the precipitate, notably bismuth, a not uncommon constituent of our Western ores.

When the sulphate of lead is impure, the precipitated lead comes down in separate pieces which are with difficulty made to cohere, or the complete precipitation may even be prevented. The presence of bismuth especially is likely to prove vexatious and vitiate correct results if proper precautions for its total elimination from the sulphate of lead are not taken. The deportment of bismuth in solutions is so interesting that a mention of its behaviour, where it exists as sulphate, may be of interest.

L. Laurent observes that there exist two sulphates of bismuth, the one soluble and the other insoluble in water. If bismuth be dissolved in boiling nitric acid and sulphuric acid added to the solution, there is at times an abundant precipitate produced, and at others none whatever. The precipitate may be easily soluble in small quantities of water, and again remain entirely insoluble, no matter how much water be used. These phenomena are dependent upon the relative amounts of free sulphuric acid present when the sulphate of bismuth is formed, and the temperature of the solution. If sulphuric acid be added to a cold solution of nitrate of bismuth, care being taken to prevent the mixture from becoming heated, no precipitate will be produced. If an excess of sulphuric acid should have been added, a sulphate of bismuth will be deposited in crystalline needles, which is scarcely soluble in sulphuric acid, but extremely so in water. If, however, a solution of this salt be heated, whether the quantity of water be large or small, a sulphate of bismuth will again be gradually precipitated which is insoluble in either hot or cold water, even if a considerable quantity of sulphuric acid should have been added.

I have found that the difficulty in regard to effecting a complete solution of bismuth may be obviated if, in the treatment of ores and metallurgical products, a large excess of sulphuric acid is added to the nitric acid solution, so that, when the evaporation takes place and the sulphuric acid fumes appear, the mass will still be in a fluid and not in a pasty condition. If the mixture is then allowed to cool, and cold water added gradually to prevent heating, all of the bismuth goes into solution and remains so for a sufficient length of time to allow a filtration and separation from the sulphate of lead to be effected.

Another impurity not unlikely to contaminate the sulphate of lead, if sufficient excess of sulphuric acid is not added, is antimony. Such antimony would also be reduced to the metallic state in conjunction with the lead by the zinc. However, in re-effecting the solution of the lead by nitric acid, the antimony would remain as the insoluble oxide and thus be eliminated.

The following experiments demonstrate that even considerable quantities of bismuth and antimony, when originally present, do not essentially affect the accuracy of the process. Five portions of lead were weighed out, and to these, severally, 100 m.grms. each of metallic antimony and bismuth were added:—

Exp No.	Weight of lead taken. M.grms.	KMnO used. C.c.	Weight of lead found.	Percentage obtained.
18	215.44	41.9	214.91	99.76
19	232.21	45.1	231.36	99.63
20	258.58	50.1	257.01	99.38
21	244.50	47.6	244.18	99.86
22	250.74	48.5	248.80	99.22

The average percentage obtained being 99.57.

In ordinary practice such combinations as given in the experiments just noted are hardly likely to be met with, and the results obtained are an ample demonstration of

the sufficient accuracy of the method for all technical purposes.

In the analysis of ores and furnace products the following plan of operation has been found most suitable:—

Place 1 grm. or 0.50 grm., according to richness of the material, in a four-inch casserole; add 15 c.c. concentrated nitric acid and 15 c.c. concentrated sulphuric acid; cover with watch-glass and heat on a hot plate until the decomposition is effected, and the fumes of sulphuric acid appear. Remove and cool; when cool, gradually add about 50 c.c. of cold water, heat to boiling, and immediately filter. Wash well with boiling water slightly acidified with sulphuric acid, and finally with plain hot water. Now rinse the insoluble residue into a beaker of about 200 c.c. capacity, using not more than 50 c.c. water; add 5 c.c. concentrated hydrochloric acid, cover with watch-glass, and boil briskly for five minutes. The sulphates of lead and lime pass into solution.

If much silica and sulphate of barium be present, it is well to filter and wash well with boiling water. If such filtration is undertaken, it must be done rapidly. Small amounts of silica do not interfere, but larger quantities prevent the subsequent precipitation of the lead in one spongy mass.

Dilute the solution with water to about 100 c.c., keeping it hot, but not boiling. Now add 2 grms. of granulated zinc. The lead begins immediately to be deposited as a metallic sponge. When the action of the acid on the zinc has apparently ceased, add an additional 0.50 grm. After five minutes the solution is again boiled for a few minutes, and then 10 c.c. concentrated hydrochloric acid added. This dissolves the remainder of the zinc very quickly, and when the reaction is completed the lead sponge will be found floating on the surface of the liquid. Decant solution, wash the lead sponge with cold water, and press it out flat with the finger. Dissolve it in 1 c.c. concentrated nitric acid and 20 c.c. hot water. Add now a slight excess of carbonate of sodium (the salt is preferable to the solution), and re-dissolve the precipitated carbonate of lead by adding 5 c.c. strong acetic acid; add 20 c.c. of 95 per cent alcohol, heat the solution to 65° C., and precipitate the lead with a saturated solution of pure crystallised oxalic acid. The lead comes down at once as a dense white crystalline precipitate. Stir briskly until the precipitate settles rapidly, leaving a perfectly clear supernatant liquid. Filter and wash precipitate three times with a hot mixture of alcohol and water (1:1), and then four times with hot water alone. (In washing the precipitate it is well to use a fine jet, keeping the stream on the filter and not allowing it to flow on the glass, as otherwise the precipitate is apt to creep upon the funnel, and thus occasion loss). When thoroughly washed, the precipitate is rinsed into a flask or beaker with about 50 c.c. hot water, 5 c.c. concentrated sulphuric acid added, and the oxalic acid determined by permanganate of potassium solution in the usual way.

The only precautions to be observed are those which have already been mentioned with reference to bismuth, and when large amounts of silica or sulphate of barium are present.

As the ratio of the atomic weight of lead to that of the combined oxalic acid is very high, any error occurring in the titration will be magnified. It is advisable, therefore, to use quite dilute solutions of permanganate of potassium, the strength of this being not greater than 1.58 grms. KMnO₄ to one litre, which will give a strength of solution, 1 c.c. equals about 50 m.grms. of lead.

The standard of the solution in terms of lead is obtained by multiplying the standard in terms of crystallised oxalic acid by 1.6428.

The time involved in the execution of the method on a single assay occupies from thirty-five to forty minutes, and the carrying out of a number of assays simultaneously is easily feasible.

The following results indicate what concordance can be obtained by the method:—

Exp. No.		Per cent.
23.	Broken Hill ore	27.61—27.50
24.	Silver precipitate of leaching process	28.86—28.75
25.	Oxidised ore	2.56—2.66
26.	Galena associated with pyrite and chalcoppyrite	22.25—21.95
27.	Galena ore (gravimetric, 66.75 per cent of lead)	66.58—66.66
28.	Oxidised ore	41.04—41.29

GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 127).

AFTER attaching the oxide of copper and the water-receptacles, several litres of hydrogen were allowed to pass through the cold apparatus to make sure of every trace of enclosed air being eliminated, and only then the gas under the reduction-tube was lighted. As soon as the oxide of copper comes up to a certain temperature, which lies below redness, the hydrogen current collapses—the gas being converted completely into water by the first short layer of oxide which it strikes against. While the formation of liquid water progresses, the water-receptacle lies in an ice-bath to minimise the weight of water which passes into the U-tube; but as soon as the oxide appears to be completely reduced, a water-bath of the temperature of the laboratory is substituted, so that as little as possible of the vapour of water in the apparatus is driven out into the air, while the water expands in rising up to the temperature of the balance.

The experiment requires constant attention, but could not be said to be difficult of execution. When all the oxide of copper has apparently suffered reduction to metal, the process is continued for a while to make sure that the reduction really is complete; the lamps under the magnesia bath are then turned off, and hydrogen is allowed to pass through the apparatus until the copper is quite cold. The reduction-tube and the water apparatus are then detached from the rest of the apparatus and prepared for the balance by passing a current of vitriol-dried air through them to expel the hydrogen. The water receptacle is then closed by an indiarubber cap at the outlet end, and by means of a closely fitting though not ground in stopper, as shown by Fig. 4, the reduction-tube by its stopper and cap as explained before, the U-tubes by turning their stoppers. The weighings are effected in the way already explained.

Before attempting a real synthesis we carried out those “blanks” and *quasi*-“blanks” which were detailed in the section on Dumas’s work, and, to us, served as useful rehearsals.

The results of our syntheses proper are given in the following table, which includes all the experiments which we made, except one or two which had to be stopped in their middle on account of breakdowns; the table, in other words, includes all those of our experiments which were really completed. In a publication like the present, it is not right to exclude any experiment or experiments, because the result is not to the taste of the experimenter; but, on the other hand, *he* is the only person competent to say which of the results should be “blackened.”

As our table gives only the net weights, we will give all the details of one of the experiments:—

Experiment VIII.

Weight of reduction-tube + oxide of copper.. .. .	tare + 36.3740 grm.
Weight of reduction-tube + metallic copper	tare + 19.2814
Hence, oxygen S, uncorrected	17.0926

* *Proceedings of the Philosophical Society of Glasgow.*

Water-flask after the experiment..	tare + 25.3239
Water-flask before the experiment	tare + 6.1363
Hence, liquid water.. .. .	19.1876 = w_0
First U-tube following the water-flask after the experiment	tare + 9.1488
The same before the experiment ..	tare + 9.0970
Hence, condensed steam	0.0518 = w'
Second U-tube (H_2SO_4), after the experiment	tare + 2.6812
The same, before	tare + 2.6805
Hence, condensed steam	0.0007 = w''
Third U-tube (P_2O_5), after	tare + 1.0499
The same, before	tare + 1.0496
Hence, condensed steam	0.0003 = w'''
Hence, water-weight uncorrected = $w_0 + w' + w'' + w'''$	= 19.2404 = W
Oxygen-weight uncor. = S =	17.0926
Hence, W - S (hydrogen) = ..	2.1478 = h

Hence $h : S = 0.12566$, whence (for $O = 16$) $H = 1.00526$.

In this experiment, for the first time, phosphoric anhydride tubes were used in conjunction with vitriol-tubes for drying the gas after leaving the copper-gauze tube and water receptacle, respectively. In all the preceding experiments, only two successive U-tubes with vitrioled pumice were used at either place. The above number (w''') shows that, in Experiment 8 at least, the P_2O_5 -tube might have been dispensed with.

In the following table, the headings of the columns refer to the *Proc. Phil. Soc. of Glasgow*; S stands for loss of weight suffered by the oxide of copper through its reduction to metal; w_0 for the weight of the liquid part of the water; w for the water collected in the U-tubes attached to the water-receptacle; W for $w_0 + w$; H for the uncorrected atomic weight of hydrogen referred to $O = 16$.

Table of Results.

Page ..	68	70	72	74	76	78
No. ..	(1)	(2)	(3)	(4)	(5)	(6)
S	4.26195	6.71315	5.53935	10.03585	10.3715	10.5256
w_0	4.7604	7.5038	6.20145	11.20945	11.6055	11.7933
w	0.0376	0.0465	0.03575	0.0838	0.0673	0.0500
W	4.7980	7.55025	6.2372	11.29325	11.6728	11.8433
H	1.0061	0.9977	1.0080	1.0024	1.0037	1.0015
Page 80	82*	84	86	88	90	92
No. (7)	7.a	(8)	(9)	(10)	(11)	(12)
S	10.4243	17.0926	18.5234	16.2367	15.4598	17.11485
w_0	11.6902	19.1876	20.78495	19.09975	17.3691	19.2266
w	0.0415	0.0528	0.0494	0.04065	0.03325	0.0365
W	11.7317	19.2404	20.83435	19.1404	17.40235	19.2631
H	1.0033	1.00526	0.9981	1.4307	1.00527	1.0041

* A break-down.

Summary.

Uncorrected Values for H Found.

(No. 10 excluded.)

No.	H.	No.	H.
2	0.9977	12	1.0041
9	0.9981	11	1.0053
6	1.0015	8	1.0053
4	1.0024	1	1.0061
7	1.0033	3	1.0080
5	1.0037		

Mean of the 11 values = 1.0032.

Probable error of a single determination = ± 0.0021 .

Probable error of the mean = ± 0.00064 .

The value W : S, even if taken in its empirical sense, is infected with an error which we had no idea of when the experiments were made; we refer to the presence of sulphurous acid in the hydrogen used. The quantity of this impurity per litre of gas used could not have been as great as in Dumas’s case, because the two vitriol tubes

which followed our copper-gauze tube were very small compared with Dumas's. To form an idea of the probable magnitude of our error, we calculated the experiments tabulated under heading III., as so many determinations of the sulphurous acid per litre of total hydrogen used, taking every grm. of oxygen used in a synthesis as corresponding to 1.5 litres of hydrogen, measured moist over water at (we said) 15° and 748 m.m. dry gas pressure. The results varied from a very small negative quantity to 0.217 m.grm. as a maximum, the mean was 0.082 m.grm.* Assuming that the SO₂ in all the hydrogen used in the syntheses just tabulated amounted to 0.2 m.grm. per litre, we arrive at H₂O : O = 1.12506, or H = 1.0005 as corrected numbers. But 0.2 m.grm. per litre is more than the hydrogen can be assumed to have actually contained; hence the proper mode of interpreting the result is to say that the true value for W : S lies somewhere between 1.12506 and 1.1254, or that of H between 1.0005 and 1.0032. But, whichever value we choose, we must correct it for the air displaced by the copper and copper oxide, and for the air displaced by the water. Strictly speaking, each of our experiments should be corrected by itself; but, considering that our values for H oscillate between 0.9977 and 1.0080, it suffices to correct their mean, or to view the eleven experiments as, so to say, *one* experiment and correct its result.

In the eleven experiments which we allowed to vote, the total quantities of oxygen, water, and, by difference, hydrogen found, were as follow:—

Oxygen.	Water.	Hydrogen.
126.0624	141.8667	15.80435

Or, reducing to 1 grm. or 8 grms. of oxygen, respectively—

1	1.125369	0.125369
8	—	1.00295

Leaving the sulphurous acid on one side for a moment, we must now reduce both the oxygen and the water to the vacuum.

The Oxygen.—Duplicate determinations of the specific gravities of the oxide of copper used, and of a specimen of the reduced copper obtained in an experiment gave the following results:—For the copper, 8.6959 and 8.7074—mean 8.7016; for the oxide, 6.1417 and 6.1420—mean 6.1418. In all the four determinations the temperature was 15°; yet we may, without committing a serious error, read the specific gravities as giving the weights of 1 c.c., and take the volume of 1 grm. of oxide of copper as = 0.16282 c.c., and the volume of 1 grm. of metallic copper as = 0.11492 c.c. The oxide of copper, however, was not pure CuO, but something between it and Cu₂O. The composition of the oxide, passing from experiment to experiment, was not by any means constant, but in one it was ascertained to correspond to the formula O + 1.0985 Cu. Assuming this formula and the above specific volumes to hold all round, we have, per 16 grms. of oxygen, for the volume of the oxide of copper, 14.850 c.c., for that of the metal 8.912 c.c., hence for the volume of the oxygen 5.938 c.c.; but this volume of air of 15° and 760 m.m. pressure weighs 5.938 × 1.2267 m.grms. Hence, for 1 grm. of oxygen the correction is +0.4553 m.grm., and this added to the above 1 grm. gives 1.000455 grms. as the true weight of the oxygen. The 1.125 grms. of water displace 1.38 m.grms. of air, hence the true weight of the water = 1.12675 grms. Hence we have, for 1 grm. of oxygen, 0.12624 grm. of hydrogen, and for 8 grms. of oxygen, 1.0099 = H grm. Allowing 0.0014 for the sulphurous acid we have H = 1.0085 ± 0.0014, on account of the *uncertainty* in this correction. But, unfortunately, this is not the whole of the uncertainty, for this reason: in the first instance, that the oxide of

copper and the metallic copper must both be presumed to have contained absorbed gases which were weighed as so much oxide and metal respectively. Hence, when we came to carry out our second series of syntheses (which we projected as soon as we had discovered the reducing action of hydrogen on vitriol), we decided upon weighing our oxygen in the Dumas fashion, and did so (*vide infra*); and after the completion of that second series, it struck us that we might utilise the reduction-tube used in it for a summary determination of the *full* correction which the oxygen weights of the first series are liable to. For this purpose 115 grms. of the kind of oxide of copper which had been used in the second series were placed in the reduction-tube and subjected to exactly the same sequence of operations as would have been involved in a synthesis of water, with this difference only, that the oxide as well as the metal was weighed twice, namely, once in air against an open tare-tube, and once *in vacuo* against another, close, tare-tube. In the case of the metal the weighing in air came last, and it must be stated that the hydrogen-vacuum was *just undone and no more* by letting in dry air before the tube went to the balance. Two experiments were made in this manner, each with very nearly, but not exactly, 115 grms. of oxide. The results were as follow:—

Weight of Oxygen Found.

	Experiment I.	Experiment II.
S, from weighings in air,		
uncorrected	21.5128	20.6520 grm.
S ₀ , by weighings <i>in vacuo</i> . .	21.5322	20.6727 „
Hence, S ₀ - S =	0.0194	0.0207 „

—or, taking for each of the two quantities, the mean of the two experimental numbers, S = 21.0824, S₀ = 21.10245, S₀ - S = 0.02005, whence—

$$\frac{S_0 - S}{S} = 0.000950,$$

or 0.950 m.grm., for the weight of air displaced by 1 grm. of oxygen; and it is perhaps as well to note that the result would have been the same, practically, if the metal, previous to its first weighing, had been allowed to take up a few m.grms. of atmospheric oxygen. The above calculation, based on our determinations of the specific gravities of the oxide and metal, gave only 0.4553 m.grm.—a very considerable difference which cannot be explained by observational errors, nor by the admitted fact that the oxide used throughout the syntheses was not constant in its composition, and even that used for the specific gravity determination was not proved to have the composition O + 1.0985 Cu adopted for the calculation of the correction for 1 grm. of oxygen, because we may well presume that the value of a given quantum of oxide of copper, which contains a small excess of metal (over and above that corresponding to CuO), is very nearly the same as if the surplus copper were present as a mere admixture of reduced metal. If we are right so far, then we have for the volume of O + *n*Cu grm. of *this* kind of oxide the equation, 0.11492*n*Cu + *x* = 0.18926(*n*Cu + O), where *x* stands for the volume of O = 16 grms. of oxygen. For the volume of 1 grm. of oxygen we have—

$$\frac{x}{16} = 0.1628 + 0.1893n,$$

and for the weight of air displaced by 1 grm. of oxygen at 15° and 760 m.m., the same × 1.2267 m.grm. Hence, by computation—

For <i>n</i> =	Weight of air displaced by 1 grm. of oxygen.
1	0.4319 m.grm.
1.0985	0.4553 „
1.2585	0.4925 „

We have reason to assume that 1.258 was about the maximum value which *n* ever assumed in the course of

* The determinations here referred to have since been re-calculated, and suffered considerable corrections, yet we retain the result feeling sure that 0.2 m.grm. of SO₂ per litre is about as good a guess as it is possible to make.

our syntheses, and yet the corresponding air displacement (0.4925) is still far below the value 0.95 found by direct experiment. The difference, great as it is, must be charged against the absorbed gases.

The S of the syntheses, however, is liable to an additional correction, because in these the metallic copper, before being weighed, was exposed to a long-continued current of dry air, from which it must be presumed to have taken up, however small, a quantity of oxygen chemically. For a guess at the probable magnitude of this error, we re-heated the metal obtained in Experiment I. in hydrogen, and next re-weighed it *in vacuo*. We then allowed 4.5 litres of dry air to pass over it, and weighed it in an air-vacuum. As a last step, the vacuum was undone by admitting hydrogen, this hydrogen pumped out, and the metal weighed in a hydrogen vacuum. We found, for the *weight of the tube and contents*—

(1) Pure copper in hydrogen vacuum	tare + 8.0012 grms.
(2) Slightly oxidised copper in an air vacuum.. . .	tare + 8.1056 „
(3) The same in a hydrogen vacuum.. . . .	tare + 8.0153 „

From (1) and the mean of (2) and (3) we have weight of oxygen absorbed as $\text{Cu}_2\text{O} = 14.25$ m.grm.

To utilise the present experiment as a means for correcting the oxygen weights found in the syntheses, let us assume that the metallic copper obtained in the first test experiment, after having been weighed (as pure Cu) *in vacuo*, had been allowed to combine with 14.25 m.grm. of oxygen before being weighed in air. The uncorrected oxygen weight then would have been $21.5128 - 0.01425$ grm., but the true value S_0 would have been the same as reported. Hence (substituting the means of the two values S_0 and S for those found in Experiment I.), we have—

Faulty oxygen weight, S =	..	21.06815 grms.
True oxygen weight, $S_0 =$..	21.10245 „
Hence, $S_0 - S =$..	34.30 m.grms.

—and, consequently, for the correction per $S = 1$ grm. the value + 1.6281 m.grm. From our notes concerning the volumes of air which, in the syntheses, were passed over the metal to be weighed, we conclude that in these the weight of oxygen taken up by unit of copper was less than it was in the test-experiment; we, therefore, now proceed to correct the data afforded by the sum of the syntheses on the basis of three successive assumptions.

I.—The oxygen taken up amounted to 14.25 m.grm. per $S = 21.068$ grm.

	Oxygen.	Water.	Hydrogen.
Uncor. numbers, as above	I	1.125369	
Corrections	+ 0.001628	+ 0.001382	
Corrected numbers	1.001628	1.126751	0.125123
Or reducing to $S_0 = 1$,	I	—	0.124920

whence $H_0 = 0.99936$.

II.—The oxygen taken up amounted to 7.0 m.grm. per $S = 21.068$ grm.

	Oxygen.	Hydrogen.
Corrected numbers	I	0.125309

whence $H_0 = 1.00247$.

III.—There was no oxygen taken up at all.

	Oxygen.	Hydrogen.
Corrected numbers	I	0.125681

whence $H_0 = 1.00545$.

If our guess at the correction for the sulphurous acid be correct, each of the three numbers for H_0 must be diminished by 0.0014, but *this* correction, under the circumstances, is not worth applying.

(To be continued).

NOTE ON THE DETECTION OF BROMINE, CHLORINE, AND IODINE IN THE SAME MIXTURE.

By F. P. DUNNINGTON.

IN the article of Mr. Lyman F. Kebler (*Four. Anal. App. Chem.*, vi., 569) upon this subject, he gives a *resumé* of the methods employed, and alludes to the necessity of employing soluble haloid salts for the most satisfactory of the processes.

For some years I have with satisfaction used a method which I have recently put in print in the second edition of Professor F. P. Venable's "Qualitative Analysis," 1892, p. 46. It is as follows:—From a solution acidified with nitric acid precipitate the silver salts of these acids with silver nitrate solution; having filtered off and washed this precipitate, treat it in a test glass with a few drops of very dilute sulphuric acid and a bit of zinc; when the dark spongy mass of metallic silver is formed, pour off the solution of the zinc salts and examine it for iodide, bromide, and chloride by the method of Professor Edward Hart.—*Four. Anal. App. Chem.*, vol. vi., p. 611.

A Novel Theory of Dyeing.—It is well known that two theories have been maintained in explanation of the process of dyeing. According to the one—the so-called mechanical view—the process is a simple absorption, similar to that by which animal charcoal takes up gases and liquids and retains them in its pores. The other theory, traces the phenomena of dyeing to definite combinations. Neither of the above theories is perfectly satisfactory. In consequence, M. Witt has put forward a theory in which he assimilates tinctorial operations to the phenomena of solution, or, in other words, to combination in indefinite proportions. He maintains that the colouring-matter is dissolved in the fibre, which becomes dyed only if its affinity for the colouring-matter is greater than that of the previous solvent. Thus, wool is dyed by magenta dissolved in water, but is not dyed if the colour is dissolved in pure alcohol. If the solvent powers of the fibre and of the water are approximately equal, there is established a kind of equilibrium, and the dye-bath does not become completely exhausted. If the solvent power of the fibre is less than that of the water there is no dyeing. In this case the solvent power of the water may be decreased by adding sodium chloride or sulphate, &c. Or the solvent power of the fibre may be heightened, *e.g.*, by chloring wool, or by depositing sulphur upon it, or by mercerising cotton.—E. Noetting, *Revue des Sciences*.

On Calcium Tartrate Extracted from the Dregs of Distilleries, its Determination and its Refining.—Ch. Ordonneau.—The author took up the idea some years ago to extract the tartaric acid from the residues of wine-distilleries in the form of calcium tartrate. He infers, on statistical evidence, that if these residues had been utilised in the Charentes in, *e.g.*, 1875, tartaric acid could have been obtained sufficient for the demand of the whole of Europe. M. Ordonneau gives a method for the determination of tartaric acid more accurate than the Goldemberg process. This process will be inserted in full.—*Bull. de la Soc. Chim. de Paris*, ix. x., No. 3.

THE DETECTION AND DETERMINATION OF
ARSENIC.*

By JOH. THIELE.

(Continued from p. 126).

3. On the Use of Platinised Zinc in the Marsh
Apparatus.

IN testing for arsenic with the Marsh apparatus it is universally customary to expedite the solution of the zinc by adding a few drops of solution of platinum. Thiele, however, makes the observation that this addition of platinum diminishes the sensitiveness of the reaction—perhaps in consequence of the formation of platinum arsenide—so that small quantities of arsenic may quite escape recognition. Thus, with platinised zinc, using hydrochloric acid as generating liquid, 0.05 m.grm. arsenious acid gave a moderately strong mirror, but decidedly fainter than with non-platinised zinc. If only 0.02 m.grm. of arsenious acid was present, the reaction failed entirely in nine out of eleven trials; whilst the same quantity of arsenic without platinum always gave distinct mirrors. Quite identical results were obtained with an addition of platinum and dilute sulphuric acid. The sensitiveness of the reaction cannot be here determined, as the very pure zinc employed was substantially insoluble in the absence of platinum.

Zinc may be platinised by immersion in a 10 per cent solution of platinum chloride and subsequent rinsing, or by adding 3 to 4 drops of this solution to the contents of the apparatus. Before adding the arsenical solution or substance it is necessary to wait until the platinum has been completely deposited.

4. On the Precipitation of Arsenic Acid with
Hydrogen Sulphide.

Thiele has investigated this method, and confirms essentially the results of Brauner and F. Tomicek, of Le Roy W. McCay, and R. Bunsen.

Arsenic acid is precipitated as arsen pentasulphide from an acidified hot solution of hydrogen sulphide, whilst if the current of gas is slow a mixture of pentasulphide and trisulphide is thrown down.

If, on the other hand, a solution of arsenic acid in concentrated hydrochloric acid is treated in the cold with a rapid current of sulphuretted hydrogen we obtain a mixture of pentasulphide with sulphur and trisulphide.

According to the author's experiments arsenic acid is thrown down from a hot hydrochloric solution partially as sulphide, even with a rapid current of hydrogen sulphide if the gas is diluted.

J. Mayrhofer has made the observation that arsenic acid is reduced to arsenious acid by highly concentrated hydrochloric acid. According to an experiment of the author's no appreciable reduction of the arsenic acid takes place at the ordinary temperature if it is dissolved in hydrochloric acid of specific gravity 1.15.

Concerning the determination of arsenic by its quantitative volatilisation as arsenic hydride, numerous experiments have been made which so far have not led to any satisfactory results. F. W. Schmidt (*Zeit. f. Anorg. Chemie*) has resumed the experiments, having observed that the arsenic in commercial zinc powder may be completely volatilised as arsenic hydride by treatment with hydrochloric acid.

In the first place the proportion of arsenic in the zinc powder was accurately determined as follows:—

Ten grms. zinc powder were cautiously dissolved in concentrated nitric acid, which was then expelled by evaporation with concentrated hydrochloric acid on the water-bath. After reducing the arsenic acid with ferrous chloride (according to E. Fischer), the arsenic was distilled over with hydrochloric acid and determined in the distillate both gravimetrically as trisulphide, and in a

second experiment volumetrically with iodine solution. The quantity of arsenic was found by both methods as 0.04 per cent.

For determining the arsenic by volatilisation as hydride the following apparatus was employed. It consisted of a globular funnel, holding 200 c.c., fitted with a tube funnel and a gas delivery pipe leading to three absorbent vessels, each of 100 c.c. capacity. Caoutchouc stoppers were used. The gas delivery tube does not project into the flask, but its aperture is in one plane with the lower surface of the stopper; the delivery tubes have a pointed end.

The round flask is placed on a water-bath in order to assist the reaction by heat. The distance of the first absorbent vessel from the globular flask was at least 20 c.m., so that the liquid is not heated in the absorbent vessel, which might easily occasion the formation of arsenic acid. The first absorbent vessel was half filled with solution of silver nitrate of the strength 1:50; the second with silver nitrate at 1:10; and the third contained bromine-hydrochloric acid.

Ten grms. of commercial zinc powder were then weighed into the globular flask. After the substance had been moistened with water, the apparatus was put together, hydrochloric acid was gradually introduced through the dropping tube—1 vol. concentrated acid to 1 vol. water—and allowed to flow down to the zinc powder. The gas evolved at once deposited black metallic silver in the first flask. When the escape of gas began to grow sluggish the flame was lighted under the water-bath. When the zinc powder was completely dissolved a slow current of hydrogen washed in silver nitrate (1:10), and consequently free from arsenic, was introduced (keeping the globular flask heated) for half an hour in order that the last traces of arsenic hydride may be removed from the flask. The contents of the third absorbent vessel and of the globular flask were found perfectly free from arsenic hydride. Hence all the arsenic had escaped in combination with hydrogen, and the transformation of the arsenic hydride with the silver solution was completed in the second absorbent flask, so that the third contained no trace of arsenic. The excess of silver was removed from the contents of the first and second absorbent vessels by means of a solution of sodium chloride, and the filtrate from the silver chloride was titrated for As by means of decinormal solution of iodine after the addition of sodium hydrocarbonate. In this manner there was found a proportion of arsenic in the zinc powder of 0.04 per cent, which agrees with the result of the gravimetric method.

The complete volatilisation of the arsenic from the zinc powder in the state of arsenic hydride depends probably on the circumstance that the arsenic in the zinc powder is present as zinc arsenide or in a very finely-divided metallic condition, which especially favours the quantitative conversion of arsenic into its hydrogen compound. A quantitative volatilisation of the arsenic must therefore be possible in other cases if the arsenic could be brought into a state analogous to zinc arsenide or into a very fine state of metallic division.

(To be continued).

Certain Molecular Compounds of the Amines.—W. Rednew.—According to the author, a close examination of these molecular compounds may throw a clearer light on the difference between these and ordinary atomic compounds. The molecular compounds are distinguished from many ordinary compounds by the circumstance that in the latter the atomic compounds originally present in their components remain unaltered. Hence it is plain that, e.g., ammonium chloride cannot be regarded as a molecular compound, whilst certain compounds of ammonia with metallic salts are probably molecular compounds.—*Journ. Prak. Chemie*, xlvii., Part 5.

* From the *Zeit. Anal. Chemie*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 2nd, 1893.

Dr. J. H. GLADSTONE, F.R.S., Vice-President, in the Chair.

MESSRS. T. K. ROSE, K. K. KACKER, and C. M. LUXMOORE were formally admitted Fellows of the Society.

It was announced that the following additions to the by-laws proposed by the Council would be presented for consideration at the coming General Meeting.

1.—In By-Law XI., after the words "The ordinary Scientific Meetings of the Societies shall be held twice in every month, from November to June inclusive, except in the month of January, when the Society shall meet once only," to add the words "and also at Easter, when, if the Council see fit, there shall also be only one meeting in the month."

2.—In Bye-Law XIII. to add the following paragraph:—"At all General Meetings of the Society, whether annual or extraordinary, no motion of a proposal to alter the by-laws shall be considered of which due notice has not been given, at least 14 days previously, either at an ordinary Scientific Meeting, or through the agency of the *Proceedings*, or by means of a printed notice addressed to all the resident Fellows."

Attention was directed to the following resolutions passed at a meeting held on March 1st, 1893, at the Royal Agricultural Society's rooms, H.R.H. the Prince of Wales, K.G., in the Chair:—

"That, having regard to the great national importance of the series of experiments which have been carried on at Rothamsted during the last 50 years, it is desirable that some public recognition should be made of the invaluable services thus rendered to agriculture by Sir John Lawes, and also by Dr. Gilbert, who has been associated with the experiments during the whole period.

"That, with this object, subscriptions, to be limited to two guineas, be invited from all interested in agriculture, whether scientific or practical.

"That, in the opinion of this meeting, the testimonial might advantageously take the form of (1) a granite memorial, with a suitable inscription, to be erected at the head of the field where the experiments have taken place; (2) addresses to Sir John Lawes and Dr. Gilbert, accompanied (if funds permit) by a commemorative piece of plate."

Ordinary certificates were read for the first time in favour of Messrs. John Charles Burnham, 179, Griffin Road, Plumstead; James Cameron, Nobel's Explosive Co., Polmont Station, A.B.; Henry Williamson Dixon, 258, Hunslet Road, Leeds; Thomas Edwards, Brewery House, Rhymney; Hedley Gordon Jones, 15, Rectory Place, Woolwich.

Of the following papers, those marked * were read:—

*121. "The Magnetic Rotation and Refractive Power of Ethylene Oxide." By W. H. PERKIN, Ph.D., F.R.S.

The following values are recorded in the paper:—

$d \ 4^\circ/4^\circ = 0.8989$; $d \ 7^\circ/4^\circ = 0.88654$; $d \ 7^\circ/7^\circ = 0.8867$; $d \ 10^\circ/10^\circ = 0.8824$.

Molecular magnetic rotation at $8^\circ = 1.935$.

Molecular refraction at 7° , $A = 17.680$.

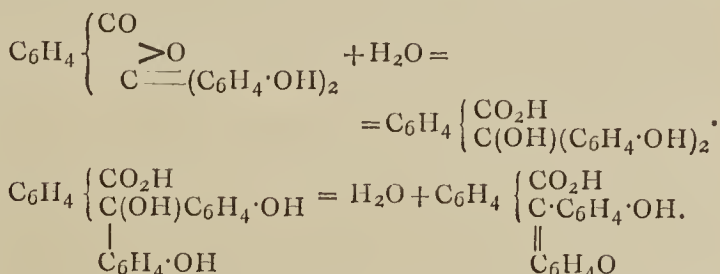
Dispersion, $G - A = 0.5494$.

It is pointed out that the magnetic rotation is most remarkably low, and the refractive power also below the calculated value ($A = 18$).

*122. "The Origin of Colour (including Fluorescence). VII. The Phthaleins and Fluoresceins." By HENRY E. ARMSTRONG.

In the first of these communications on the origin of colour (*Proc. Chem. Soc.*, 1888, No. 4, p. 27), exception was taken to the formulæ assigned to phenolphthalein and its congeners. Although the exhibition of colour by these substances could not be accounted for by the formulæ ascribed to them, the data then available were insufficient to permit of more satisfactory formulæ being devised. The subsequent discovery of the rhodamines strengthened this conviction, and the intention to make these the subject of experimental study as soon as an opportunity occurred has long been kept in mind; fortunately this is no longer necessary, the technical value of these substances having led to their further investigation in various works laboratories, with the result that they have been shown, as was anticipated, to exhibit properties proving that they also are quinonoid compounds.

The *Chemiker Zeitung*, No. 104, December 28, 1892, contains an account of a communication made to the Heidelberg Chemical Society on December 16, by Prof. Bernthsen, who points out that the rhodamines afford true ethereal salts when subjected to the conjoint action of alcohol and chlorhydric acid: in other words, that they afford carboxy-compounds and not lactone derivatives. After directing attention to other evidence in favour of the view that the colours of this class are members of the triphenylmethane group, he points out, in so many words, that the characteristic development of colour on adding alkali to phenolphthalein is, in all probability, due to the fact that the colourless lactone phenolphthalein is thereby hydrolysed and converted into a quinolic compound, which suffers dehydration, affording a coloured quinonoid compound:—

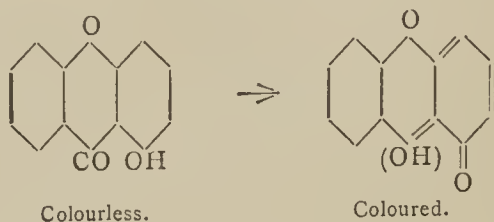


In a more recent paper (*Berichte*, 1893, 172), Friedländer—who does not appear to be aware of Bernthsen's communication, has stated that phenolphthalein and hydroxylamine readily interact in an alkaline solution and form a hydroxime; this and other evidence he mentions leads him to express the opinion that in their coloured state phenolphthalein and the allied phthaleins which behave similarly in presence of alkali are all quinonoid compounds.

But, as so frequently happens at the present day, the patent literature contains statements which anticipate the views of Bernthsen and Friedländer, *c.g.*, a description being given of the formation of ethereal salts of rhodamines by the action of alcohol and chlorhydric acid in the French patent specification No. 224603, of the "Farbenfabriken vormals Friedr. Bayer und Co." (Elberfeld), dated September 28, 1892. It is pointed out in this specification that the rhodamines are to be regarded as carboxylic compounds, and the absence from the ethereal salts of the property which the rhodamines exhibit of forming salts and lakes is referred to as confirmatory of this view.

Friedländer is led to regard the fluoresceins as perhaps different from the phthaleins, as he was unable to obtain hydroximes from them, and speaks of their colour as conditioned by their xanthone-like structure. There appears to be no reason, however, why a distinction should be drawn between the intensely fluorescent rhodamines and the analogous oxygenated compounds—the fluoresceins.

Even regarding them as xanthone derivatives, the appearance of colour in these latter is, it can scarcely be doubted, consequent on the occurrence of isodynamic change (*cf. Proc. Chem. Soc.*, 1892, 103).



The problem, therefore, remains practically the same; nevertheless, there can be little doubt that the phthalein-fluorescein group still offers interesting matter requiring further study.

Perhaps the point of chief interest claiming attention is the extraordinary ease with which the hydrolysis of the lactone is effected in the case of phenolphthalein, as evidenced by the fact that it is among the most sensitive of the known indicators of alkali: in contemplating the changes which may attend the dissolution of substances by water, such facts are undoubtedly of high importance. Perhaps the change is less a consequence of the instability of the lactone ring, and is mainly conditioned by the hydroxyl present in the para-position relatively to the carbon atom to which the phenolic radicles are attached—it is conceivable that a hydrated metallic derivative of the phenol is initially produced, and that the metal and water necessary to effect the hydrolytic change are thus brought into the intramolecular sphere of interaction. From this point of view it would be interesting to determine the degrees of readiness with which phthalid and its various derivatives undergo hydrolysis. It is also worth noticing that, according to Bernthsen, the anhydrous rhodamine base forms a colourless solution in benzene, and may be obtained in large colourless crystals, while its solution in water is coloured, and it forms an intensely coloured pentahydrate.

The recognition of the quinonoid character of such eminently fluorescent substances as the fluoresceins and rhodamines may be claimed as a most important argument on behalf of the view that fluorescence is a form of colour: indeed that, taken in conjunction with other facts, it goes far towards justifying the contention that all quinonoid derivatives would be visibly fluorescent, were it not that, as in the case of certain quinine salts, as Hartley has pointed out, the rays which are the cause of the fluorescence sometimes become absorbed in the solution.

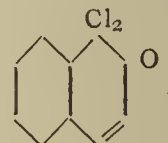
*123. "The Origin of Colour. VIII. The Limitation of Colour to Truly Quinonoid Compounds. Change of Colour as Indicative of Change of Structure, as in the case of Alizarin." By HENRY E. ARMSTRONG.

A quinonoid compound may be defined as a *hexaphene*, i.e., an unsaturated cycloid composed of six "elements" (*cf. Proc. Chem. Soc.*, 1892, 129), two "elements" of which are $C\equiv R''$ groups in either para- or ortho-positions.

Coloured substances generally appear to fall within this definition, as there do not appear to be any established cases of the existence of coloured substances (a) containing a single $C\equiv R''$ group, or (b) in which two such groups are present in a cyclane or saturated ring, or (c) in which the cycloid contains any other number of elements than six. The succinosuccinic derivatives, &c., are but apparent exceptions to b, as those which are coloured may be regarded as isodynamic forms of the saturated compounds. Diacetyl and dibenzoyl (benzil) may be mentioned as exceptions to the general definition, but for this very reason it appears likely that they will eventually be obtained colourless; it is easy to account or the appearance of colour in diacetyl, as it undergoes condensation with extreme facility, yielding dimethyl-

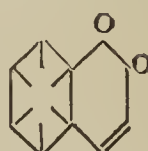
quinone (paraxyloquinone), an intensely yellow substance. Such a change is not likely to occur in the case of benzil, but this compound is so faintly yellow that the colour may well be due to impurity.

Some of the keto-chlorides described by Zincke appear to be exceptions to a, e.g., the compound—

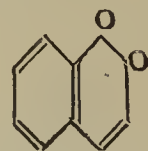


prepared by chlorinating betanaphthol, the colour of which is a yellow of considerable intensity, and there is no reason to suppose that this is not characteristic of the pure compound. It is not improbable, however, that the group CCl_2 in this and similar substances may be the true equivalent of a $C\equiv R''$ group. In an article on "The Determination of the Constitution of Carbon Compounds from Thermochemical Data," published in the *Phil. Mag.*, in February, 1887, summarising and briefly discussing the results described in the fourth volume of J. Thomsen's *Thermochemische Untersuchungen*, it was suggested that the greater development of heat which attends the formation of symmetrical dichloro-derivatives may be due to the partial neutralisation of the (residual) affinity of the one chlorine atom by the other: in other words, that chlorine atoms are possessed of the power of directly entering into association while combined with another atom, in which case $2Cl$ would be the equivalent of R'' .

As the presence of two ortho- or para-carbonyl groups in a saturated ring apparently does not condition colour, it would seem that the two $C\equiv R''$ groups are concerned together with the "ethenoid linkages" in the unsaturated ring in the production of colour; hence, the fact that compounds such as the naphthaquinones and the keto-chloride before referred to are coloured is of importance, as evidence that perhaps a single ethenoid linkage in the ring is sufficient, and that it is not necessary that there should be two such, symmetrically situated with reference to the two $C\equiv R''$ groups as in the benzoquinones; this, however, is on the assumption that the naphthaquinones are derivatives of *centric* and not of *ethenoid* benzene, hence the perhaps; the importance of this consideration will be more clearly realised after reference to the arguments made use of in the two following notes:—

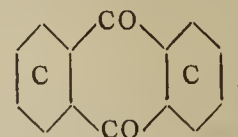


"Centric" β -naphthaquinone.



"Ethenoid" β -naphthaquinone.

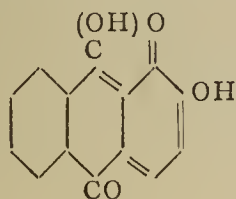
Anthraquinone—which, it may be remarked, has scarcely any of the properties of a true quinone—may be referred to in this connection: if represented as a derivative of *centric* benzene, thus—



the median group would appear to be saturated; yet, as anthraquinone may be regarded as formed by the superposition of benzene and quinone, it would seem that the median group is still possessed of quinonoid characteristics; unless it be that the effect of the two CO groups is supplemented by that of the two symmetrically placed centric cycloids.

It would seem appropriate to here direct attention to the colour of alizarin in comparison with that of anthraquinone. The colour of paraquinones and their deriva-

tives, in all cases in which the structure appears to be in no way open to question, is uniformly yellow; and red is characteristic of orthoquinones. How comes it then that alizarin is red? The conventional formula is not in accord with this fact, but the colour may be accounted for by regarding alizarin as an isodynamic form of dihydroxyanthraquinone, *e.g.*,



On this assumption there is no difficulty in understanding why the monhydroxyanthraquinones are of no use as dye-stuffs; and why the introduction of two contiguous hydroxyls into anthraquinone is of such importance; furthermore, it is to be expected that a monethoxy-derivative prepared from alizarin if it contained an α -ethoxy-group would resemble anthraquinone while one containing a β -ethoxy-group would more nearly resemble alizarin in colour: and, as a matter of fact, two such compounds have been described, one of which is yellow and the other red.

In like manner it may be suggested as probable that the chloranilates are not derivatives of paraquinone, and that their formation involves the occurrence of isodynamic change, thus:—



The arguments advanced in proof of their paraquinonoid nature do not appear to be in any way conclusive. Lastly, reference may be made to the *phenoquinones* and *quinhydrones*: it is difficult to regard these as being other than members of that ill-understood and vaguely-defined class of substances termed molecular compounds. If so, the changes in the colour of quinones involved in their formation may arise from the weighting of the $C\equiv R$ groups by the attachment thereto of the phenol.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 10, March 6, 1893.

Analysis of the Ash of the Diamond.—Henri Moissan.—All the samples of bort and of diamonds from the Cape which we have examined contained iron which formed the chief part of the ash. It has also been found in the ash of carbonado and of Brazilian diamonds, except a variety of bort of a green colour, which is totally free from it. In all the samples silicon has been detected, and in most of them calcium.

Certain New Properties of the Diamond.—Henri Moissan.—The temperature of the combustion of the diamond varies with different specimens; it fluctuates between 760° and 875° . In general the harder a diamond the higher is its temperature of combustion. If a diamond resists at 1200° chlorine, hydrofluoric acid, and the action of different salts, it is, on the contrary, easily attacked at

this temperature by the alkaline carbonates, and this decomposition in a gaseous form has enabled us to prove that the specimen studied contained neither hydrogen nor hydrocarbons.

New Derivatives of Phenolphthalein and Fluoresceine.—A. Haller and A. Guyot.—This memoir is not adapted for useful abstraction.

Election of a Foreign Associate vice Sir Richard Owen.—Sir Joseph Lister was elected by a large majority. He received 46 votes as against 6 given to Baron Nordenskiöld and 5 to Mr. Newcomb.

Industrial Preparation of Alumina.—A. Ditte.—Bauxite is treated with caustic soda, the aluminate obtained is mixed with a small quantity of crystalline alumina, and the solution of aluminate is treated in the cold with a current of carbonic acid, which gives rise to a precipitate of aluminium hydroxide easily washed. At the end of some hours there remains merely a small quantity of alumina in solution.

The Isomerism of the Amidobenzoic Acids.—Oechsner de Coninck.—The author has studied the solubility of the three acids in different media; in the hydracids, in certain oxacids, both mineral and organic, and in certain media having an alkaline reaction.

Dimorphism of Dimethylamine Chloroplatinate.—Le Bel.—It appears that among the chloroplatinates of the amines, the dimethylamine compound forms various double salts, and, in particular, that it unites in equal molecules to that of dipropylamine, forming a double salt remarkably well crystallised. A mixture of the dimethyl- and diethylamine-chloroplatinates merely furnishes the compounds of dimethylamine and diisobutylamine. The power of forming double salts seems therefore restricted to very special terms.

On Inuline and Two New Proximate Principles: Pseudoinuline and Inulenine.—C. Tanret.—The composition of inuline is $C_{72}H_{62}O_{62}$. It is very soluble in hot water, but requires more than 10,000 parts of cold water for solution. It is also readily soluble in hot weak alcohol. Its aqueous solutions are very limpid and not opalescent like those of leucogen, to which they have been erroneously compared. Baryta-water dissolves inuline at first, but a further addition precipitates the compound $C_{72}H_{62}O_{62}BaO$. This reaction is very sensitive, and is given very distinctly by a solution of inuline at 1:600th. Pseudoinuline has the composition $C_{192}H_{102}O_{102}$. Its barium compound is more soluble than that of inuline, whence a solution of pseudoinuline at less than 3 per cent is not precipitated by baryta-water. Pseudoinuline is not precipitated by lead subacetate without an addition of ammonia. Inulenine has the composition $C_{120}H_{104}O_{104}$. Cold baryta-water dissolves inulenine without the formation of a precipitate by an excess, but it is thrown down by luke warm concentrated solution of baryta.

Absorbent Action of Cotton on Dilute Solutions of Mercuric Chloride.—Léo Vignon.—The author has formerly shown (*Comptes Rendus*, Feb. 10 and April 28, 1890) that animal fibres have definite chemical functions, basic and acid, whilst vegetable fibres display feeble chemical functions and especially no basic functions. Cotton must therefore be considered as a feeble acid, the chemical function of which becomes more intense as the proportion of oxycellulose increases. The author has now extended these ideas to the absorbent action of cotton on dilute solutions of corrosive sublimate. The mercury chloride in which the cotton has been steeped is impoverished in mercury. The cotton combines with mercuric oxide, whilst it is merely impregnated with hydrochloric acid without entering into combination. The author intends to determine if the mercury is fixed upon the cellulose as oxide or as oxychloride, and if a part of the mercury thus fixed passes into the state of mercurous chloride.

Remarkable Resistance of Goats to the Effects of Morphine.—L. Guinard.—Whilst 0.0003 grm. per kilo. of live weight narcotises a man, a proportion one thousand times greater is easily endured by goats.

Perfumes of the Orchids.—Eugène Mesnard.—One and the same flower of an orchid emits decidedly different odours, according as it is observed in the morning or at night, as it has been exposed to the sun or kept in the shade, as it has been gathered when freshly opened or is fading. A very remarkable periodicity has even been observed in the development of the perfume of certain orchids. M. Mesnard admits, however, that he cannot at present submit any hypothesis in explanation of this phenomenon.

Journal für Praktische Chemie.
New Series, Vol. xlv., Parts 5, 6, and 7.

Researches on Alloisomerism.—Arthur Michael.—Already inserted.

On the Methylnaphthalines.—Gustav Wendt.—This memoir is chiefly a critique on a paper in the Berlin *Berichte* (xxiv., 3918) by Prof. H. Wichelhaus.

The Double Haloid Compounds of Gold.—Emil Petersen.—On the action of a rapid current of chlorine upon finely divided gold without the aid of external heat, but with retention of the heat of the reaction, there is chiefly formation of Au_2Cl_4 , with smaller quantities of a trichloride. Au_2Cl_4 , on treatment with refrigerated alcohol, gives off to the latter trichloride, whilst there remains monochloride, which latter, on the prolonged action of alcohol, is partially resolved into gold and trichloride. Krüss and Schmidt propose to eliminate Au_2Cl_4 and the corresponding bromine compound from the series of gold compounds. The author, however, insists on their retention as true chemical compounds chiefly on thermochemical evidence.

Researches from the Laboratory of the University of Freiburg.—Ad. Claus.—The author criticises the recent treatise of Grimaux (*Comptes Rendus*) on the quinine iodomethylates, and discusses the relations of quinine, quinidine, cinchonin, and cinchonidine.

Condensation of β -Diketones with Urea and Thio-urea.—P. Evans.—A preliminary communication.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements after Easter:—John Macdonell, three lectures on "Symbolism in Ceremonies, Customs, and Art"; Professor R. K. Douglas, three lectures on "Modern Society in China"; E. L. S. Horsburg, three lectures on "The Waterloo Campaign"; Professor Dewar, five lectures on "The Atmosphere"; R. Bowdler Sharpe, four lectures on "The Geographical Distribution of Birds"; James Swinburne, three lectures on "Some Applications of Electricity to Chemistry" (the Tyndall Lectures); Henry Craik, C.B., three lectures on I. "Johnson and Milton," II. "Johnson and Swift," III. "Johnson and Wesley"; Dr. A. C. Mackenzie, three lectures on "Falstaff," a Lyric Comedy, by Boito and Verdi (with Musical Illustrations, by kind permission of the composer and publishers, Messrs. Ricordi, specially granted for these lectures). The Friday Evening Meetings will be resumed on April 14th, when a Discourse will be given by Sir William H. Flower, K.C.B., on "Seals"; succeeding Discourses will probably be given by Professor A. B. W. Kennedy, Professor Francis Gotch, Mr. Shelford Bidwell, The Right Hon. Lord Kelvin, Mr. Alfred Austin, Mr. Beerbohm Tree, Professor Osborne Reynolds, Professor T. E. Thorpe, and other gentlemen.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Testing for Cotton in Woollen Goods.—(Reply to F. S. C.)—The usual and best reagent is caustic potash or soda, which dissolves the wool and leaves the cotton. Use a solution of 1.02 sp. gr.; boil for 15 minutes, wash, and dry carefully. For details see *CHEMICAL NEWS*, vol. xlv., p. 262, and vol. l., p. 123.—P. D. R.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Medical, 8.30.
Chemical, 8. (Annual Meeting). President's Address. Election of Office Bearers and Council.
TUESDAY, 28th.—Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30.
Photographic, 8.
WEDNESDAY, 22nd.—British Astronomical Association, 5.

ERRATA.—In the Report of the Physical Society, p. 131, col. 2, line 25 from top, for "reserved" read "reversed." Line 52, for "optical" read "special." P. 132, col. 1, line 17 from bottom, for "size" read "sine."

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THE CHEMICAL NEWS.

VOL. LXVII. No. 1740.

ON THE ORIGIN OF COLOUR.

IV. VIBRATIONS. BREAK-ETHERS. OXYGEN.

By WILLIAM ACKROYD.

(Concluded from p. 111).

No cause has been assigned that I am aware of for what Sorby has termed "the band-raising power" of solvents (*Proc. Roy. Soc.*, xxi., 1873, p. 443). The theory of vibrations has been applied by Carnelley (*Phil. Mag.*, 1884, pp. 139 and 140), and previously by Houston and Thompson (*CHEMICAL NEWS*, xxiv., p. 188), to explain the colour changes of solids and liquids. In my paper on "Metachromatism" (*CHEMICAL NEWS*, xxxiv., p. 77), I have attempted to show that "atomic potentiality" is the only necessary concomitant of colour change,—a view which brings the phenomena within the bounds of allotropy and isomerism. Now, as then, I am persuaded that writers have not acquainted themselves with the infinitesimal nature of the vibrations they have called to their aid in attempting to explain colour change. The following example will illustrate my contention.

Silver iodide above its point of maximum density, 116° C., expands upon being heated with the normal order of colour change; thus from yellow at 116° it becomes gradually darker until at 180° it is orange-red; at 412° a dark brick-red, and at 450° a dark red liquid. Now what increase in amplitude of molecular vibration is there in changing, say, from yellow AgI at 116° C. to the red salt at 216° C? Rodwell gives good reasons for assuming that a volume of 1·00000 at 116° C. becomes a volume of 1·01455238 at 450° C. (*Proc. Roy. Soc.*, No. 157, 1875). Therefore a row of AgI molecules, 1 c.m. long at 116°, will have increased to 1·001452 c.m. at 216° C. In this row there will be from one hundred millions to two thousand million molecules according to Lord Kelvin's estimate. Hence it follows that one of these molecules through a range of 100° during the change of colour from yellow to red is not disturbed from its relative position with regard to the others, in round numbers, more than a thousandth of a tenth-metre, or, say, five-millionths of the length of a wave of light. While not denying that vibrations of this order of magnitude may have a marked effect in the absorption of light, and also be the cause of fluorescence in bodies exhibiting this phenomenon, I am disposed to look for the origin of colour to the more proximate cause of molecular aggregates.

In the length of an ether-wave, a thousand molecules can be ranged, and I shall here advance the view that aggregates of thousands of these molecules are required to dissipate the ether-waves in producing selective absorption like masses of rock breaking up the sea-waves. It may indeed be that just as the stillness of a Norwegian fjord as compared with the turbulence of the outer ocean is produced by the natural break-waters of the outlying islands, so the ethereal tranquillity within a coloured body, denoted by absorption of light, may be due to these natural break-ethers of molecular aggregates.

The nearest approach to this conception would be that of a liquid with minute particles in suspension and exhibiting phenomena such as I find a solution of sulphuretted hydrogen exhibits. When it is first prepared, and for a few days afterwards, it presents the following appearances when viewed by transmitted diffused daylight.

First day Yellow.
Second day Blue with yellowish reflection.
Fourth day Sea-green with pinkish reflection.

And as the particles settle it is finally without colour. This phenomenon, with occasional variations in the nature and order of colour change, is best seen with the soft moorland waters in use here; with harder well-waters the deposition of suspended particles is more rapid and the colour effects not so marked. We may perhaps regard the first effect as being due to the action of particles of three different orders of size on the light; as one of these subsides the next effect is blue, and finally, as none but the finest particles are left, the liquid appears sea-green. If these particles could be sorted out and framed into a thin film of transparent solid, one can readily conceive of the last subsiding particles—break-ethers pure and simple—yielding a body which appears sea-green by transmitted light and has a pinkish surface reflection.

In transparent coloured solids and in coloured solutions, however, there is no break of continuity. The break-ether is not distinguishable with the eye or with the most powerful microscope; prismatic light alone detects it. My observations go to prove that it is of the same order of magnitude as the ether wave itself. Thus we have seen that the beginnings of absorption in iodine violet solutions, or, in other words, the width of the break-ether of iodine, is 4000 tenth-metres.

Taking 5000 tenth-metres as a near approach to the mean length of a luminiferous ether wave, we may employ this as the unit in estimating the sizes of break-ethers. I have made the following determinations in the manner described for iodine:—

	Size of break-ethers (unit 5000 tenth-metres).
Iodine, in violet solutions .	0·80
Potassium permanganate (3 central bands)	0·26
Magenta	0·09
Iodine green	0·96
Methyl violet, 3 B	0·12

These substances exhibit isolated absorption-bands. The numbers vary with the intensity of the light used and with the dispersive power of the spectroscope. I have employed a paraffin oil lamp and a Browning's spectroscope with single dense glass prism.

The break-ether in yellow solutions or transparent solids will show its influence first in the violet or ultra-violet region of the spectrum; a number of them yielding absorption up to F give the following figures in the above units:—

Iodine in yellow solutions	2·4
Bichromate of potash	20·0

The "band-raising" power of different solvents in dissolving the same body, regarded from the break-ether standpoint, resolves itself into a difference of disintegrating or adhesive power of the solvents—one solvent producing smaller break-ethers than another. A comparison of violet iodine with violet iodine solutions (*CHEM. NEWS*, lxvii., p. 111) shows that the general absorption of the latter is raised towards the violet end of the spectrum, presumably because the break ethers of the dissolved iodine are of different size from those of the gaseous element.

The possible constitution of a break-ether has been shown in my note on the "Atomic Colour Cross" (*CHEM. NEWS*, lxv., p. 205). It is built up of atomic material of definite distribution in the table of the periodic or natural classification of the elements.

An increase in number of break-ethers increases the absorption of light (*CHEM. NEWS*, O&A. 5, 1877). The number may be increased either by (1) rise of temperature—the usual colour-changing phenomena; (2) increase of stratum, or depth, or strength of substance through which light is passing; or, (3), by changes similar to that of solid platinum or silver to the black finely-divided element obtained by chemical means.

Somewhat similar molecules, *i.e.*, molecules akin as in a natural series of compounds, constructed on the same

plan, and varying in volume in definite order, must, one may presume, form similar aggregates of the break-ethers, varying but slightly, and that in gradations of dimensions such as to regulate the absorption of light in definite order, and therefore producing colour in definite order, and the relations of colour to constitution.

Since writing the first of these papers, the researches of Dewar have directed special attention to the properties of liquid oxygen. With its blue colour it falls naturally into its place in the sulphur series of elements (CHEM. NEWS, lxxvii., p. 27) and also shows the relation of atomic volume if we take Wroblewsky's figure for the specific gravity, viz., 1.24 at -200°C. , the lowest temperature at which the sp. gr. appears to have been taken (*vide* Clarke's "Constants of Nature," Part I, p. 8).

Halifax, March 20, 1893.

THE DETECTION AND DETERMINATION OF ARSENIC.*

By JOH. THIELE.

(Concluded from p. 142).

IN the first place the attempt was made to determine 0.12 grm. of arsenious acid in the apparatus, and by the method described with the use of 30 grms. pulverised zinc. The first absorbent vessel was charged with a solution of silver at 1:50, the second and the third with silver solutions at 1:10. On titrating the contents of these vessels with decinormal solution of iodine according to the method described, there was found only 95 per cent of the arsenic present, so that about 5 per cent remained in the generating-flask.

The result was quite different if a hydrochloric solution of stannous chloride was added to the contents of the flask through a tube funnel after the lapse of about an hour when the development of hydrogen is nearly at an end. In the moment when this solution fell into the clear liquid of the round flask there appeared a turbidity and then a dark precipitation. This turbidity and precipitate disappeared in a few minutes on adding a little platinum chloride to revive the liberation of hydrogen, and the liquid resumed its former appearance. Hereupon the flask was heated for about fifteen minutes, and a current of hydrogen free from arsenic was passed through the apparatus for the same length of time.

On determining the arsenic in the absorbent vessels, the entire quantity of arsenic was found, and the residue in the generating flask was found to be entirely free from arsenic.

The method conducted as just described allows, consequently, of a quantitative determination of the arsenic, and may be especially important in judicial investigations.

The author leaves it undecided whether on the addition of stannous chloride there takes place a combination of the metallic arsenic deposited with the precipitate of spongy tin forming tin arsenide, or whether the arsenic is present in the tin sponge in a finely divided metallic state.

The author has modified the apparatus above described as follows:—The round flask, containing 300 c.c., was connected with a Woulfe bottle holding 150 c.c., its gas inlet tube being provided with a Bunsen valve or a glass ball valve. This renders a reflux impossible, so that it is not necessary to observe the working of the apparatus continually. The Woulfe bottle was connected with three receivers holding 100 c.c. each, all containing solution of silver at 1:50, the Woulfe bottle containing as much as corresponded to the arsenic used for the experiment. The further precaution was taken that all the liquid was forced through the dropping funnel into

the round flask by the pressure of hydrogen, whereby the ascent of gas bubbles into the dropping funnel is made impossible.

If the zinc used in the experiment is not perfectly free from arsenic, its proportion can be easily determined in the above apparatus and deducted from the results of the several experiments.

The author purposes ascertaining whether the method cannot be used for separating arsenic from antimony or for determining both elements when jointly present.

THE ABSORPTION OF FREE NITROGEN BY PLANTS.

As soon as organic analysis was rendered capable of accuracy, a number of interesting questions could not fail to be raised. One of the most important—the weightiest, in fact—from a practical point of view, was the origin of the nitrogen found in plants. We weigh, *e.g.*, the total crop of wheat, or of beans, produced upon an acre of land. We take a fair average sample of the bulk, or, for the sake of greater accuracy, a number of such samples, and we determine with every precaution their percentage of combined nitrogen. From the result it is easy, of course, to calculate how much nitrogen has been present in the entire crop. Now comes the question: Whence have the plants obtained this nitrogen? We analyse the seed, and find a certain amount. We analyse in like manner the soil, including the manures which have been used. We determine the ammonia present in the air, in the rain, and in the ground-water. We add together all these quantities of combined nitrogen, and we find that the sum falls very considerably short of the combined nitrogen present in the crop.

This fact is fully recognised by Sir J. Lawes and Dr. Gilbert as a conclusion drawn from their prolonged and world-famed researches, and they admit that there must exist in nature a source of nitrate which science has not yet discovered, or, it might be added, has not yet appreciated.

As a confirmation of this truth, our attention is drawn to Alpine pastures. Their supply of nitrogenous matter is constantly drawn upon in the form of milk and cheese. Still the grass continues to grow and to nourish the cattle, although no nitrogenous manures—such as guano, nitre, ammonium sulphate, &c.—is ever applied. To say that the fertility of the soil is kept up by the dung and urine of the cows—as farmers of the old school still believe—is in reality to affirm the creation of matter. The excreta in question cannot possibly contain anything other or more than there was in the grass, *minus* the quantity sent away in the form of dairy produce. Hence the question is narrowed. Either the nitrogenous matter is obtained from the superabundant stock of free nitrogen existing in the atmosphere, or it must have its source in some unknown product, not hitherto identified, either in the soil, the air, or the water. But such a product, such an *x*, to play so wide and important a part, would have to exist, not in minute traces easily overlooked, but in relatively large quantities.

Hence we are driven back upon the free nitrogen of the atmosphere as the only conceivable resource: and here we enter the realms of the controversy. Men of science have, quite justifiably, demanded positive proof that the nitrogen of the air is thus absorbed and assimilated. The necessary experiments are, of course, delicate and tedious, and without special precautions it is worse than useless.

One of the earliest experimenters in this direction was the celebrated Boussingault, who, as early as 1838, recognised the free nitrogen of the air as one of the three sources whence plants derived their supply of nitrogen. The other two sources admitted were the ammonia existing in the atmosphere—which is manifestly insufficient

* From the *Zeit. Anal. Chemie*.

—and the dust suspended in the air—a supply which can scarcely come into serious consideration.

At this time M. Georges Ville took up the subject. In his experiments he showed that the nitrogen found in the plants exceeded, by several thousand times, the quantity which they could derive from atmospheric ammonia: and, as for dust, it was carefully excluded by special arrangements. Consequently, the nitrogen found in the crop in excess of that existing in the seeds could be due only to a fixation and absorption of the free gaseous nitrogen of the air.

It might have been expected that Boussingault would have welcomed M. Ville's verification and extension of his results. Nothing of the kind. Though the discovery of the assimilation of free nitrogen by plants had opened to him the doors of the Academy—though Dumas (*Comptes Rendus*, vi., p. 131) had accepted the proof that "clover absorbs the nitrogen of the air, and everything leads us to believe that this phenomena is general," yet, in 1852, Boussingault read before the Academy of Sciences a voluminous memoir in which he repeated *seventeen times* the words "the nitrogen of the air is not absorbed by plants." Yet all the time he proclaimed it an injustice when he was accused and convicted of this remarkable change of front. He asserted (*Comptes Rendus*, xxxviii., p. 719) that if he had proved anything in his former memoir it is that the gaseous nitrogen of the air was not fixed by vegetation in his last experiments.

Fortunately, in the scientific world at least, when a man formally eats his own words and denies what he has formerly asserted, and what has been accepted as his title of honour, he cannot carry the world with him. The late Abbé Moigno (*Cosmos*, iv., p. 561) thus clearly expounds the case:—

"1. The assimilation of the gaseous nitrogen of the air by plants, although M. Boussingault's demonstration was incomplete, was made known with such characters of evidence, surrounded with such a total of irrefragable confirmation, that it has been accepted with such a rational enthusiasm as to make it more than rash to seek at present to call it in doubt.

"2. The method of experimentation followed by Boussingault in his first experiments has been proclaimed so rational and so certain in its fundamental arrangements, so exact in its results, that, especially since M. Ville has so modestly completed it, so skilfully freed it from all the objections which might still be raised against it, there can no longer remain the shadow of a doubt as to the absolute reality of the fact which it places in evidence.

"3. Lastly, the new method followed by M. Boussingault is as bad as his first method was good if we suppose it completed. His recent experiments are as futile and as barren of conclusions to be drawn from them as his earlier experiments, when rightly interpreted, were convincing and fruitful."

We have yet to show in detail the misleading character of the later experiments undertaken by M. Boussingault.

THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Continued from vol. lxvi., p. 228.)

SOME time ago we contributed an article on this subject,† and we now propose to complete our remarks on the question. In the former article we dealt with the subject in an introductory manner, and we now propose to discuss it in detail.

The complete practical analysis of iron and steel, as generally understood, comprises the determination of

silicon, sulphur, phosphorus, combined and graphitic carbon, manganese, and, in some instances, of copper, titanium, chromium, tungsten, and oxide of iron. Before proceeding with the description of the methods employed for the determination of these several constituents, we wish to draw the operator's attention to two points which it is necessary to rigidly observe before results that can lay any claim to accuracy can be obtained, viz.:—(1) The reagents employed must be absolutely pure; and (2) strict cleanliness and the avoidance of dust, which, unless due precautions are taken, will accumulate during ignition, weighing, &c.

Silicon.—In the methods employed for the estimation of silicon in iron and steel, it must be oxidised into silica (SiO_2), and then collected and weighed. When the metal is treated with aqua regia or nitro-hydrochloric acid, the iron enters into solution as ferric chloride, while the silicon is oxidised into silica, which, upon evaporation of the solution and strong heating, is rendered insoluble.

As nitro-hydrochloric acid is constantly employed in the analysis of iron and steel, &c., a stock should be prepared. It is made by adding one part of pure nitric acid (sp. gr. 1.42) to three parts of pure hydrochloric acid.

For analysis, 4 gms. of the sample in the state of drillings should be carefully weighed out into a porcelain dish of 500 c.c. capacity, covered with 50 c.c. of nitro-hydrochloric acid, the mouth of the dish being covered with a large watch glass to prevent loss by spurling, and the whole heated gently on a hot plate or sand bath. When the iron is of such a nature as will not allow of the sample being obtained as drilling, as, for instance, white iron, it should be reduced to a fine powder in a steel mortar. Some chemists advise that the drillings should be treated with boiling ether under a condenser, and subsequently dried at 100°C ., the object being to extract the oil, grease, &c., with which it may have accidentally become contaminated. This is hardly necessary if ordinary care be exercised during its preparation. Silicon and graphite—especially the latter—appear to be unevenly distributed in grey pig iron. The drillings from such must therefore be very carefully mixed. Drillings not carefully mixed gave:—

	I.	II.	III.	IV.
Silicon, per cent ..	2.11	1.74	1.93	1.70
Graphite, per cent ..	3.00	3.50	3.37	3.80

Instances have been noted in which serious discrepancies have occurred between chemists, arising solely from the assumption that the sample of pig was of even composition throughout, and that drillings taken from any part would give like results. When it is judged that the whole of the iron is in solution, the watch glass must be removed, and washed by a fine stream of hot distilled water, in order to recover any of the solution which might have spurted on to the glass. The solution is then evaporated to complete dryness and heated strongly over a Bunsen burner until the residue is black—the heat of the sand-bath or hot plate not being sufficient. When the dish and contents are thoroughly cool, the residue is moistened with 60 c.c. of hydrochloric acid, and gently heated until all the iron is brought into solution, and the excess of acid expelled from the solution by carefully evaporating until a crust commences to form. At this point evaporation must be arrested, and the crust dissolved by the addition of a few drops of hydrochloric acid. To the solution thus obtained, five times its volume of hot distilled water are added, and the whole filtered through a good English filter-paper previously washed three times with a dilute solution of hydrochloric acid and several times with water. All filter-papers, previous to being used, should be subjected to this washing with acid and water. The paper retains the residue, consisting of silica (SiO_2) and, perhaps, graphite. The portions of the residue adhering to the sides of the dish are detached by

* From *Industries*, January 27, 1893.

† See *Industries*, vol. vii., p. 211; also *CHEMICAL NEWS*, vol. lxvi., p. 228.

means of a "policeman," *i.e.*, a piece of caoutchouc tubing at the end of a glass rod, and rinsed into the filter. The filter-paper and contents are then washed, four times with a hot 10 per cent solution of hydrochloric acid, and afterwards repeatedly with water until a drop of the washings gives no red colour when brought in contact with a 5 per cent solution of sulphocyanide of potassium, several drops of which have been placed on a white porcelain slab. If a steel be under examination, the residue on the filter consists of silica (SiO_2); but if an iron, graphite or graphitic carbon is generally also present. The treatment of the filter and its contents depends therefore upon whether one or both of these constituents are present. If silica only be present, the filter-paper and contents are transferred to a porcelain or platinum crucible, ignited at a strong red heat, and, when cold, weighed. The weight, minus that of the filter-paper ash, gives the silica (SiO_2), which contains 46.66 per cent of silicon.

Several of the constituents of iron and steel are present in such minute quantities that an increase or decrease amounting to 1 or 2 m.grms. in the weights of the precipitates obtained in their determination make a considerable difference in the resulting percentages. It therefore becomes necessary to determine the amount of ash contained in the filter-paper employed, and to deduct it from the weights of the precipitates obtained.

In the presence of graphite, the filter-paper and contents are placed in a shallow porcelain dish, and the paper burnt off at the lowest heat possible (a high temperature would result in the graphite being burnt off also). When cold, the residue, consisting of silica and graphite, is weighed, replaced in the dish, and again ignited, this time at a bright heat. The graphite burns off, while the silica remains behind. When cold it is weighed and the amount deducted from the combined weights of the silica and graphite, the weight of the graphite thus being obtained.

Great difficulty is experienced in obtaining a pure white silica by this method, it being usually more or less coloured. This is especially the case with specimens containing considerable quantities of phosphorus, and it is then due in all probability to an insoluble phosphide of iron (Riley, *Chemical Journal*). Neither can the whiteness of the silica be taken as a guarantee of its purity, as, although free from iron, it may at the same time be contaminated to a considerable extent with titanium, if that metal is contained in the iron or steel. To obtain the silica in a pure state it is transferred to a platinum crucible, intimately mixed with six times its weight of acid potassium sulphate (KHSO_4), and fused. Upon cooling, the fused mass is broken up as completely as possible with the aid of a glass pestle. The crucible and contents are then placed in a porcelain dish and digested for a considerable time while constantly stirred with cold water. When the whole of the fused mass has dissolved, the crucible, after being well washed, is withdrawn, and the residual silica, now free from impurities, collected on a filter; or the silica may be volatilised by gently heating in a platinum crucible with hydrofluoric and sulphuric acids (both are essential), the residue weighed, and the silica estimated by difference.

The following method, while occupying considerably less time in its performance, furnishes results nearly as accurate as the one just described:—Four grms. of the sample contained in a beaker are treated with 60 c.c. of dilute sulphuric acid—1 part acid to 3 of water—the mouth of the beaker covered with a watch glass, and the whole placed on a hot plate or sand-bath. When the iron is dissolved, the watch glass, after being washed, is removed, and the solution evaporated until thick white fumes of sulphuric acid are given off. The evaporation is then arrested, and the beaker and contents allowed to cool. 100 c.c. of water are then added, and the whole heated to the boiling point, while constantly stirred, until the whole of the mass of anhydrous ferrous sulphate has been dissolved. The silica is then filtered off, together

with some graphite probably, washed, &c. The purity of the silica thus obtained is determined by the method previously described.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1893.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolitan Water Act, 1871.

London, March 12th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

As a result of the excessive rainfall of the month, the condition of the metropolitan water supply during February, though not unsatisfactory for the period of the year, was found to compare somewhat unfavourably with that manifested in January, which was on the whole a dry month, despite a fall, as measured at Oxford, of over three-quarters of an inch during the last few days of the month, and so only affecting somewhat the early supply for February. The total rainfall for February, as measured at Oxford, was 2.64 inches, being 0.72 inch above the average, and constituting the month one of the wettest Februaries recorded for several years past.

But the more or less flooded state of the rivers during a large portion of the month, though having a prejudicial influence on the supply, more especially in respect to the degree of freedom from colour-tint, did not affect the proportion of organic matter present in the water to any such extent as to bring it into appreciable excess over the low winter average prevailing during the previous two months, as shown in the following Table. Moreover the mean ratio of organic nitrogen to organic carbon, or 21.5 to 100, was low, and indicative so far of the preponderating vegetable nature of the actually small proportion of organic matter present in the supply.

Of the total 168 samples of water examined during the month, two only were recorded as deficient in brightness, the remainder, despite the flooded state of the rivers, being found to be clear, bright, and well filtered.

		Ratio of brown to blue tint.	Oxygen re- quired for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
		Means.	Means.	Means.	Maxima.
Previous	two				
months	..	23.6 : 20	0.068	0.198	0.286
January	— : 20	0.052	0.159	0.248
February	— : 20	0.069	0.201	0.269

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.

GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 141).

Second and Final Series of Syntheses.

THESE we carried out after we had learned to prepare absolutely oxygen-free hydrogen: by passing the gas (after its deoxidation by red-hot metallic copper), over fused caustic potash, followed by phosphoric anhydride (instead of over vitriol) for its dehydration.† Let us state at once that the P_2O_5 tubes never gained weight appreciably, so that, as we now know, they might have been dispensed with.

While preparing for these final experiments we invented an easy method for obtaining a very perfect vacuum, by means of two ordinary pumps. An ordinary syringe, provided with a solid piston and a two way cock at the end of the barrel, was combined with a large bottle in which a fair ordinary vacuum was maintained by a second air-pump in such a manner that the waste air from the syringe instead of being sent into the atmosphere was discharged into the vacuum-bottle. By proceeding in this manner we easily succeeded in producing a vacuum of less than 1 m.m.; and yet we soon came to give up this

rubber. The indiarubber tube is closed at its lower end by means of copper wire, M. For the tightening of the indiarubber tube at J, two pieces of copper wire of exactly the same weight were provided, one served in the first exhaustion, the other in the second. The joints were found to hold very tight, only in the first rehearsal the rim of the reduction-tube cracked in consequence of the belt of the stopcock part being pressed against it by the atmosphere. This, however, in subsequent experiments, was easily avoided by placing a few small bits of card paper between the two glass surfaces. The tare for the reduction-tube was made out of a piece of combustion tubing of the same width as that for the working-tube. This tare tube was simply drawn out and closed at both ends, but its outer volume was so adjusted that it displaced exactly the same weight of water as the working tube did with its cap and stopcock on.

We might have stated before that there is a stopper of asbestos at F, which was introduced for the first experiment and never taken out.

In a synthesis, the first step was to charge the reduction-tube with about 115 grms. of oxide of copper, and, after having attached the stopcock, to heat it in a magnesia bath in a current of dry air (about 4.5 litres). This, as a rule, was done on the day preceding the experiment. The tube was left overnight with the cock

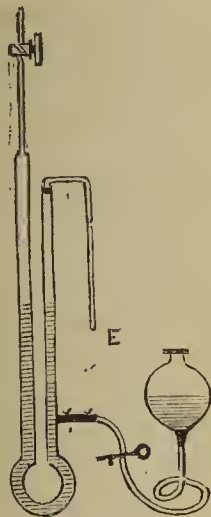


FIG. 8.

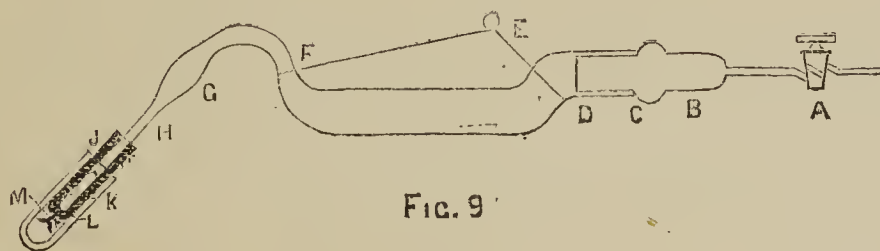


FIG. 9

refinement, because it turned out that the pump proper, when in good condition, exhausted to about 3 m.m. easily, and this sufficed for our purpose, because we took care to weigh both the metallic copper and the oxide of copper in a hydrogen-vacuum, besides measuring the pressures of our *vacua* by means of a specially constructed mercury gauge, shown at Fig. 8. (A rather large syphon-manometer, the vacuum limb of which was provided with a very good Greiner and Friedrich stopcock, while the open limb communicated with a mercury reservoir. As the tube was about a c.m. wide inside, it was easy to fill the instrument with mercury without introducing more than a trace of air, and the influence of this was reduced to a minimum by expanding the vacuum into the largest available space.) The construction of the reduction-tube is shown by Fig. 9, for the explanation of which it suffices to say that, during use, the joint at c was made tight by means of a close bandage of warm non-vulcanised indiarubber, secured by double wires both at the left and at the right of c, and that during the evacuations the end H was closed with an indiarubber cap as shown in the figure. J is a piece of red indiarubber tubing, K a rounded glass rod, L a glass cap fitting over the indiar-

closed and the cap wired on, and on the following morning it was exhausted with the pump or combination of pumps. Hydrogen was then admitted into it, and the tube allowed to stand beside the balance while the other apparatus was being weighed. It was next exhausted as completely as possible (the vacuum meter being read this time) and weighed against its tare. After the attainment of constancy of weight, the tube was left suspended for at least ten minutes, to make sure that no air leaked in. From the beginning of the first to the end of the last weighing, the indiarubber joint at c was kept covered over with a piece of very thin silver foil to prevent change of weight as far as possible. During the progress of a reduction, the parts of the tube which were not meant to be heated were protected by suitable asbestos anhydride screens.

The water-receptacle was the same as the one which had been used in the first series, except that the U-tubes which followed it were charged, the first with fused caustic potash, the second with phosphoric anhydride. On account of the bulkiness, more than on account of the greater weight, of the reduction-tube, the small balance which we had used in the first series was not conveniently available this time. We substituted for it an excellent kilo balance from Oertling, which, like the smaller instrument used before, is provided with a Dittmar microscopic reading arrangement, and which, even when charged with several hundred grms. on each side, is constant in its indications to within 0.2 to 0.1 m.grm.

* *Proceedings of the Philosophical Society of Glasgow.*

† The corresponding U-tubes were prepared in this way:—A quantity of asbestos was dehydrated by heating, then shaken in a bottle with an abundant supply of the anhydride, and quickly transferred to the U-tube after its bend had been about half filled with the reagent.

On account of the introduction of the vacuum method for the determination of the oxygen, the execution of the experiments was not quite so easy as in the first series, and it took us some time before we became quite familiar with all the manipulations involved. But there would be little use in here giving exact instructions in regard to minor details. Whoever cares to repeat our experiments must go through his own apprenticeship.

In now proceeding to report on the individual experiments, we shall, for brevity's sake, use the following symbols:—

S for the loss of weight suffered by the reduction-tube.
 m' and m'' for the tension of the hydrogen, in which the CuO and Cu were weighed, respectively.

S_0 for the corrected weight of the oxygen. As a rule $S_0 = S$.

w_0 for the uncorrected weight of the water obtained in the liquid form.

w' and w'' for the uncorrected weights of the steam condensed in the caustic potash tube following the water-receptacle, and in the P_2O_5 tube following the KHO tube respectively.

t'' for the temperature, and P'' for the pressure, of the atmosphere at the second weighings.

"Air" for the weight of air displaced by the w_0 gm. of liquid water.

W for the total weight of water uncorrected; W_0 for the same corrected.

h_0 for the weight of hydrogen $= W_0 - S_0$.

H for $8 \times (h_0 : S_0)$; that is to say, the atomic weight of hydrogen referred to $\text{O} = 16$.

Experiment (1). $S = 17.0530$; $m' = 7$ m.m.; $m'' = 5$ m.m.; hence $S_0 = S$. $w_0 = 19.0367$. $w' = 0.1457$. $w'' = \text{nil}$. Hence $W = 19.1824$; $t'' = 11.75^\circ$; $P'' = 748.9$ m.m. Hence, air displaced by the w_0 grms. of liquid water $= 23.3$ m.grm.; and $W_0 = 19.2057$, and $h_0 : S_0 = 0.126$ 236, and $H = 1.009$ 89.

There was a little difficulty in getting the last drop of water out of the drawn-out end of the reduction-tube into the water-flask; otherwise the experiment proceeded quite normally.

Experiment (2). In this experiment everything proceeded quite normally except that, at the end, when the reduction-tube and water-flasks were detached from each other, a minute drop of water was seen adhering to the end of the neck of the former. Rather than simply neglect this water, or lose the experiment, we produced as good an imitation as we could of the droplet at the end of a tared glass tube, similar to the neck referred to, and weighed it. It amounted to 4.3 m.grm. Allowing this as a correction for the water-weight directly found we had $S = 17.3342$; $m' = 3.5$ m.m.; $m'' = 5.0$ m.m. $S_0 = S$. $w_0 = 19.4403$; $w' = 0.0568$; $w'' = 0$. Hence $W = 19.4971$. $t'' = 11.5^\circ$; $P'' = 756.6$ m.m. Hence air displaced $= 24.0$ m.grm., and $W_0 = 19.5211$, whence $h_0 : S_0 = 0.126$ 161, and $H = 1.009$ 29.

If we neglect the drop of water lost we have $h_0 : S_0 = 0.125912$, and $H = 1.00731$.

Experiment (3). $S = 17.2882$; $m' = 6.0$; $m'' = 6.0$ m.m. Hence $S_0 = S$. $w_0 = 19.3892$; $w' = 0.0544$; $w'' = 0.0001$. $W = 19.4436$. $t'' = 13^\circ$; $P'' = 748.9$. Hence air $= 23.6$, and $W_0 = 19.4672$, whence $h_0 : S_0 = 0.126040$, and $H = 1.00832$.

Experiment (4) was lost through the pressure of the atmosphere driving the stopcock part of the reduction-tube against the receptacle of the oxide and causing it to crack.

Experiment (5). In this experiment the air-pump failed to work properly, so that the pressure in the reduction tube could not be reduced to less than 27 m.m. Otherwise everything went on all right.

$S = 20.3540$; $m' = m'' = 27.0$ m.m. Hence $S_0 = S$. $w_0 = 22.8360$; $w' = 0.0630$; $w'' = 0.0002$. Hence $W = 22.8992$.

$t'' = 13^\circ$; $P'' = 754.0$. Hence air $= 28.0$, whence $W_0 = 22.9272$, and $h_0 : S_0 = 0.126422$, and $H = 1.01138$.

Experiment (6). In this experiment the air-pump again failed to work satisfactorily, and, as a consequence, the two readings of the manometer were inconveniently high, and, what is worse, different from one another. The experiment otherwise proceeded all right.

$S = 20.4418$; $m' = 15$; $m'' = 40$ m.m.; corresponding correction $= +0.26$ m.grm. Hence $S_0 = 20.4421$. $w_0 = 22.9232$; $w' = 0.0565$; $w'' = 0.0002$. Hence $W = 22.9799$. $t'' = 14.8^\circ$; $P'' = 758.6$. Hence air $= 28.1$; $W_0 = 23.0080$; $h_0 : S_0 = 0.125521$; and $H = 1.00417$.

Experiment (7). $S = 20.8639$; $m' = m'' = 18$ m.m. Hence $S_0 = S$. $w_0 = 23.4059$; $w' = 0.0608$; $w'' = 0$; $W = 23.4667$. $t'' = 15.3^\circ$; $P'' = 751.7$. Hence air $= 28.4$; and $W_0 = 23.4951$; $h_0 : S_0 = 0.126112$; and $H = 1.00890$.

Experiment (8). In this experiment the reduction-tube cracked just before its second exhaustion, hence the metallic copper had to be weighed in hydrogen at the pressure of the atmosphere. We had:— $S = 20.1952$; $m' = 18$ m.m.; $m'' = 752.0$; calculated correction $= +7.4$ m.grm. Hence $S_0 = 20.9226$. $w_0 = 23.4745$; $w' = 0.0578$; $w'' = 0.0005$. Hence $W = 23.5328$. $t'' = 15.5^\circ$; $P'' = 752.0$. Hence air $= 28.4$, whence $W_0 = 23.5612$; $h_0 : S_0 = 0.126112$; and $H = 1.00890$.

Experiment (9). $S = 21.0957$; $m' = m'' = 3$ m.m. Hence $S_0 = S$; $w_0 = 23.6543$; $w' = 0.0714$; $w'' = 0$, whence $W = 23.7257$. $t'' = 15.5^\circ$; $P'' = 747.4$. Hence air $= 28.5$; $W_0 = 23.7542$; $h_0 : S_0 = 0.126021$; and $H = 1.00817$.

Experiment (10). $S = 21.8994$; $m' = m'' = 2$ m.m. Hence $S_0 = S$; $w_0 = 24.5870$; $w' = 0.0400$; $w'' = 0$. Hence $W = 24.6270$. $t'' = 15^\circ$; $P'' = 752.0$, whence air $= 29.8$; $W_0 = 24.6568$; $h_0 : S_0 = 0.125912$; and $H = 1.00730$.

Experiment (11). $S = 21.8593$; $m' = 1.5$; $m'' = 1.0$ m.m. Hence $S_0 = S$. $w_0 = 24.5407$; $w' = 0.0474$; $w'' = 0$; $W = 24.5881$. $t'' = 15.0^\circ$; $P'' = 751.5$. Hence air $= 29.8$; $W_0 = 24.6179$; $h_0 : S_0 = 0.126198$; and $H = 1.00959$.

Experiment (12). $S = 21.8499$; $m' = 2.5$; $m'' = 2.0$ m.m. Hence $S_0 = S$. $w_0 = 24.5067$; $w' = 0.0654$; $w'' = -0.0001$; $W = 24.5721$. $t'' = 15.75^\circ$; $P'' = 761.4$. Hence air $= 30.0$; $W_0 = 24.6021$; $h_0 : S_0 = 0.125959$; and $H = 1.00768$.

Experiment (13). $S = 21.5788$; $m' = 1.7$; $m'' = 2.0$ m.m. Hence $S_0 = S$. $w_0 = 24.2118$; $w' = 0.0631$; $w'' = 0$; $W = 24.2749$. $t'' = 14.9^\circ$; $P'' = 761.1$. Hence air $= 29.8$; $W_0 = 24.3047$; $h_0 : S_0 = 0.126323$; and $H = 1.01059$.

Experiment (14). $S = 20.9709$; $m' = 3.5$; $m'' = 3.7$ m.m. Hence $S_0 = S$. $w_0 = 23.5422$; $w' = 0.0461$; $w'' = -0.0001$; $W = 23.5883$. $t'' = 15.2^\circ$; $P'' = 760.6$. Hence air $= 28.9$; $W_0 = 23.6172$; $h_0 : S_0 = 0.126189$; and $H = 1.00951$.

(To be continued).

Oxidising and Decolourising Action of Charcoal.
—Cazeneuve (*Pharm. Central Halle*).—As far back as 1874 A. W. von Hofmann observed that charcoal—especially animal charcoal—can exert a strong oxidising action. An alcoholic solution of leukaniline quickly yields rosaniline if boiled with animal charcoal. Cazeneuve made similar observations on boiling aqueous solutions of α -naphthylamine or of paraphenylenediamine with animal charcoal; the first mentioned becomes a purple red and the second a brown. The charcoal retains the colour firmly, but yields it up again to boiling alcohol. The idea that the oxidising action of carbon was concerned in the decolourising action was at once suggested. On experiments made for this purpose it was found that charcoal which had been previously ignited and cooled in a current of dry nitrogen or in carbon dioxide had less decolourising power than such as has been cooled in the air. Cazeneuve is of opinion that the residual oxygen in the charcoal burns the colouring-matter.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 2nd, 1893.

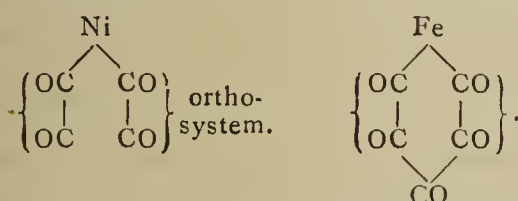
Dr. J. H. GLADSTONE, F.R.S., Vice-President, in the Chair.

(Concluded from p. 145).

*124. "Note on Optical Properties as Indicative of Structure." By HENRY E. ARMSTRONG.

In his "Notes on some Recent Determinations of Molecular Refraction and Dispersion," recently communicated to the Physical Society (*Phil. Mag.*, 1893, 203), Dr. Gladstone directs attention to a number of curiously suggestive observations of special interest in connection with the all-fascinating enquiry into the correlations of properties and structure. The metallic carbonyls to which he refers, in respect of physical properties as in many other respects, are compounds of extraordinary interest. The conclusion which both Mond and Gladstone favour that they are cycloids is undoubtedly that most in harmony with their general behaviour, affording as it does an explanation of the complete masking of the metal, comparable, for example, with that which sulphur suffers in thiophen.

The excessive refractive and dispersive power which the metallic carbonyls exhibit is probably, as Gladstone suggests, to be sought in the peculiar arrangement of the carbonyls; one object of this note is to call attention to the evidence which the optical data apparently afford of their *co operative action*. The ketonic compounds hitherto studied from which the value $\text{CO}=8.4$ has been derived have been compounds containing single or isolated carbonyls, whereas—if represented as cycloids—the metallic carbonyls contain two "ortho-systems," thus—



In this sense they are in fact diorthoquinonoid, and are comparable with coloured substances, but they are not truly quinonoid, the cycloid being saturated, and hence should not be coloured. (The nickel compound is colourless, but the iron compound is described as yellow; the instability of the latter, however, is such that this colour may be due to impurity). There are only two orthoquinonoid systems, although there are five carbonyls in iron pentacarbonyl, so that one of the carbonyls should have the ordinary value and only four the value they apparently exhibit in nickel tetracarbonyl (11.9): consequently the molecular refraction should be—

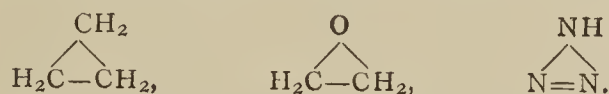
$$\begin{array}{rcl} 4\text{CO (orthoquinonoid)} & = & 4 \cdot 11.9 = 47.6 \\ \text{CO (ketonic)} & = & 8.4 \\ \text{Fe"} & = & 11.6 \\ \hline & & 67.6 \end{array}$$

a value not far removed from that found, viz., 67.4.

If this argument be a sound one, it is to be anticipated that quinonoid compounds generally will be found to possess specially high refractive powers; and there is some evidence that this is the case: thus among the compounds examined by Gladstone (*Chem. Soc. Journ.*, 1870, 101–147; *Trans.*, 1884, 241) anthracene—a hydrocarbon which, as more than once pointed out, is probably quinonoid in structure—is credited with a very high value, considerably above that calculated even if the value 6.1

be assigned to carbon. Gladstone has also stated that β -nitraniline has an abnormally high refractive power. I learn from Professor Mills that the compounds referred to as α - and β -nitraniline which he gave to Gladstone were the meta- and para-derivatives; apparently, therefore, this result is in accord with the view previously advocated (*Proc. Chem. Soc.*, 1892, 101), that paranitraniline and similar coloured nitro-compounds are in reality quinonoid. Dr. Gladstone states, however, that both substances were examined in weak solutions, and, therefore, less than the usual confidence can be felt in the accuracy of the data.

Living and Dewar's determination of the molecular refraction of nitrous oxide in the liquid state is also referred to by Gladstone, who points out that the value observed (11.418) favours the view that the nitrogen in nitrous oxide has the low value which this element exhibits in nitriles, viz., 4.1. The determination of the structure of nitrous oxide is of special importance, as it is one of a group of compounds, including trimethylene, ethylene oxide, and diazoimide, all of which it is the fashion at the moment to formulate as cycloids:—

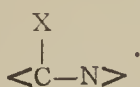


But apparently there is no valid evidence to justify the practice, and it is in no way necessary to adopt such a course. Unfortunately we are without knowledge of the optical properties of trimethylene, but we have J. Thomsen's remarkable observation that its heat of combustion exceeds that of the isomeric propylene by 6690 units. I have on several occasions discussed the properties of this hydrocarbon, and have pointed out how its unique behaviour with bromine and bromhydric acid may be explained by electrolytic considerations (*cf.* Morley and Muir's "Watts' Dictionary of Chemistry," iii., Art. "Isomerism.") Granting the accuracy of Thomsen's figures, there appears to be no way of avoiding the conclusion that it is an open chain hydrocarbon, and, therefore, that free affinities may exist at the end of a chain; its dissimilar behaviour towards bromine and bromhydric acid precludes the application of von Baeyer's explanation of the instability of a ring of three atoms, as such a ring should prove unstable to bromine as well as to bromhydric acid, the former being in all other cases the more active agent in attacking hydrocarbons.

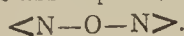
Ethylene oxide, in like manner, has an abnormally low heat of formation; in fact, on this account, J. Thomsen has gone so far as to represent it by the formula $\text{CH}_2 \cdot \text{O} \cdot \text{CH}_2$, an expression offending against all recognised canons. If, however, trimethylene be written $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$, ethylene oxide may be written $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}$. Perkin's results, referred to in a previous note (*ante*), show that it is abnormal in its optical behaviour; they are most significant as affording evidence—assuming an open chain formula—that the optical effect of free affinities is below the normal, and it may be anticipated that trimethylene will afford low values. It is worth noting that carbonic oxide, in which we believe that certain of the affinities of the carbon atom, if not free, are "self engaged," has a molecular refraction (7.5) considerably below the value of CO in ketonic compounds: it would seem that the ordinarily accepted refraction equivalents are not to be regarded as measures of the effect of the "affinities" proper, but of the affinities engaged between atoms.

Passing now to the nitriles and nitrous oxide, we have the most indefinite ideas as to the former: they are conventionally represented as compounds of triad nitrogen, but this practice is but the outcome of formal obedience to certain artificial and dogmatic rules of valency, and has no real justification. As we must admit the existence of latent affinities in carbonic oxide—which may be written <CO —we may also admit the possibility of their

existence in nitrogen, and may represent the nitriles as compounds of the form—



Nitrous oxide, on this assumption, would be—



Diazoimide might, in like manner, be regarded as—



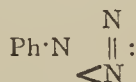
a formula which is implied in Mendeleeff's assumption that it is dinitrile. No diazoimide derivatives have hitherto been examined: Dr. Perkin had the kindness to determine the refractive power of the phenyl derivative, of which a quantity was placed at my disposal by Prof. Tilden: the results are as follows:—

$d_{10^\circ/10^\circ} 1.0980$; $d_{15^\circ/15^\circ} 1.09318$; $d_{25^\circ/25^\circ} 1.08527$.

	t .	n .	$\frac{n-1}{d}$.	$\frac{n-1}{d} P$.
A	11.7	1.54719	0.49943	60.431
C	11.7	1.55407	0.50571	61.191
D	11.7	1.56063	0.51170	61.916
F	11.7	1.57793	0.52749	63.826

Deducting from the value of aniline, 52.09, the value of two hydrogen atoms, 2.6, and adding twice the highest value of nitrogen, 2.51, the theoretical value is $A=59.89$, which is lower by 0.54 than that found; so that diazophenimide has proportionally a somewhat higher molecular refraction than even aniline.

These results do not indicate that diazophenimide is a dinitrile; neither is it possible to deduce from them any special argument in favour of the formula—



the problem, in fact, remains unsolved.

Consideration of the facts makes it appear probable that a solution of the difficulty may be found, and not only so, but that it may be possible ere long to carry on the enquiry into the inter-relationship of structure and physical properties on more fruitful lines than has of late been possible.

In the case of paraffinoid compounds generally, both carbon and hydrogen seem to have a fixed optical value, and it may be supposed also that this is true of hydrogen in all cases; seemingly also, *ethenoid carbon*—carbon as it is in ethylene, whatever may be the mode in which the atoms are united—has a constant value. The variations which are noticed in paraffinoid and ethenoid derivatives must on these assumptions be ascribed to variations in the radicles displacing hydrogen; and it should be easy therefore, by studying a considerable number of properly chosen compounds, to determine which radicles are, and which are not, subject to variation and the circumstances which condition variation.

In the case of benzenoid compounds, there is no evidence of constancy. Even in the case of the hydrocarbons the value of the C_6 group rises from $C=6$ (very nearly) in benzene to $C=6.15$ in mesitylene, the only apparent alteration made consisting in introducing methyl in place of hydrogen. As all the evidence derived from the study of paraffinoids seemingly shows that CH_3 has an invariable value, it is only logical to suppose that the variation arises in the cycloid; in other words, that whereas the ethenoid C_2 system apparently has an invariable optical effect, the benzenoid C_6 system has a variable optical effect. There is nothing surprising in this conclusion—it is in absolute accordance with the experience derived from the study of the chemical behaviour of the benzenoid compounds. The variation, in many cases, is very considerable: that of aniline, for example, which has a molecular refractive power $A=52.09$. Assuming NH_2 to be $5.1+2.13=7.7$, and

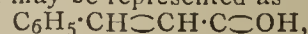
deducting the value of $5H=6.5$, the value of C_6 in aniline is $52.09-7.7-6.5=37.89$, and $C=6.31$. There is no reason why the value should not be still higher in diazophenimide: to determine the value of the N_3 , either N_3H or one of its paraffinyl derivatives should be examined. The chemical properties of diazophenimide are such—its nitro-derivatives are hydrolysed with such facility—as entirely to justify the assumption that the N_3 has a very special influence on the properties of the cycloid.

The strongest confirmation of the view here put forward is afforded by diphenyl, in which each carbon apparently has the value 6.39: the two radicles of which this hydrocarbon is composed being alike, and being both benzene residues and directly conjoined—putting the hydrogen aside—there can be no question that the variation is due to the variation in the optical effect of the C_6 group.

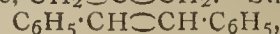
If it can thus be shown either that the ethenoid group has an invariable effect whatever number of such groups may be present in the compound, or that its effect is invariable except in certain cases in which a co-operative effect is traceable, and the benzenoid group be proved to have a variable optical effect, the most absolute demonstration will have been secured of the existence in benzenoid compounds of a peculiar structure such as is foreshadowed in the centric formula first proposed by me in February, 1887.

The following may be referred to as illustrative of the problems requiring consideration. Among haloid compounds, methylene iodide is altogether peculiar, its refraction equivalent (58.22) being much above the calculated value (52.1); this may be a case of co-operative action. The high dispersive power of carbon bisulphide is perhaps to be accounted for in some such manner. In iodoform, an eminently remarkable substance on account of its *colour* and other exceptional properties, the third iodine atom appears to exert an influence comparable with that of an ethenoid group in quinone, and to determine the appearance of colour. In this case the effect is seemingly produced within the sphere of affinity around the carbon atom, much as in the case of quinonoid compounds it is produced within the cycloid sphere of affinity. Bromopicroin, if the value found by Gladstone be correct, appears to be an example involving a negative influence, a cause which perhaps also prevails in the case of acetylenic compounds, the abnormally low refractive power of which is highly remarkable. The aldehyds offer many peculiarities. It is to be remembered that Thomsen has represented aldehyd as $CH_3 \cdot C(OH)$; the oxygen in such a compound would have a lower value than in ketones, but the one atom of carbon, being in the carbonic oxide or dyad state, would probably have a lower value than 5; so that, by assigning the full value to both carbon atoms and the ketonic value to oxygen, the equivalent would be over-estimated. But no indication that such is the case is actually afforded by aldehyd.

The refraction equivalent of benzaldehyd is about two, and that of salicylic aldehyd about three, units above the calculated value; this may be due to an increase in the cycloid value, but it is conceivable that the cycloid and the ketonic groups in some way co-operate; and it is even possible to represent salicylic aldehyd as a quinonoid compound. It is noteworthy that both these aldehyds are very active substances, and prone to yield condensation products. Cinnamic aldehyd is one of the most refractive and dispersive of known substances, and its refraction equivalent (75.3) is much above the calculated value, 65.4. It may be represented as—



or even as $C_6H_5 \cdot CH \cdot C \cdot CH \cdot OH$, and it would seem probable that the high refractive power is conditioned by a co-operative influence of the contiguous cycloid and ethenoid groups. From this point of view, it is important to examine allene, $CH_2 \cdot C \cdot CH_2$. Stilbene,—



is another equally striking instance, its refraction equivalent (113.39) being also very much higher than the calculated value (101).

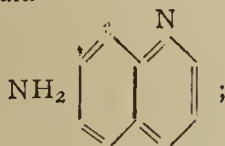
The arguments here made use of in correlating optical properties and structure are undoubtedly applicable to the discussion of other physical properties, and as some of these are apparently the measure of intra- and others of extra-molecular effects, it is all important that a careful comparison should be made with the object of elucidating reciprocal relationships.

In conclusion, attention may be directed to the anomalous colour dispersion displayed by rosaniline and other colouring-matters. In these compounds the two $C\equiv R$ groups are of totally distinct types, and apparently the effect has not been noticed in the case of compounds in which the quinonoid groups are alike or similar. Biot has shown that the phenomena of anomalous rotatory dispersion exhibited by tartaric acid solutions are simulated by a mixture of two optically active mutually indifferent substances having different rotatory dispersive powers; it seems not improbable that the two dissimilar quinonoid groups which condition colour in rosaniline and substances which behave like it condition anomalous colour dispersion in consequence of their dissimilarity.

125. "The Origin of Colour. (IX.) Note on the Appearance of Colour in Quinoline Derivatives and of Fluorescence in Quinine." By HENRY E. ARMSTRONG.

The arguments put forward in the previous note have far-reaching consequences. The increase in refractive power observed on comparing the homologues of benzene with benzene might be ascribed to a passage from the centric to the ethenoid form—assuming the former to have a slightly lower optical value than the latter; and such a view would be in accordance with the observed change in chemical behaviour, but it would not account for the change in the case of aniline and other compounds, as the optical value of carbon in these rises above that which is seemingly characteristic of the ethenoid form.

That the change takes place in some cases there can be little doubt, especially when von Baeyer's researches are taken into account. The object of the present note is to point out that its occurrence would account for the appearance of fluorescence and colour in quinoline derivatives which has been discussed in a previous note (*Proc. Chem. Soc.*, 1892, 143). Assuming quinoline to be a centric cycloid, and that the introduction of NH_2 has a very marked effect, as in the case of aniline, it is possible that the compound may thereby be caused to acquire an ethenoid structure; but such an ethenoid compound would be quinonoid, as may be seen on reference to the formula—



in other words, any amido-derivative of quinoline might be quinonoid, and therefore coloured, probably either orange or red.

In like manner, an ethenoid form of naphthalene would be quinonoid; it is therefore possible that the fluorescence exhibited by many naphthol and naphthylamine derivatives is characteristic of the pure substances, and does not always originate in impurities.

If the argument here used be justified, the non-appearance of colour and fluorescence in naphthalene derivatives will afford evidence of a centric structure similar in character to that which the peculiar optical behaviour of benzenoid compounds affords of a special structure different from the ethenoid form in benzene.

DISCUSSION.

The CHAIRMAN (Dr. Gladstone) said that he would like to consider the suggestive remarks of Prof. Armstrong on

molecular refraction more carefully before committing himself to a definite opinion; the idea of a "co-operative influence," such as had been put forward, was, he thought, worthy of all attention. It had long struck him as an unexplained phenomenon, that while in the aromatic substances in general 6.1 is indicated as the atomic refraction of each of the double linked carbons, the value was very appreciably lower in benzene itself and in toluene; and that when the compound becomes very complex, the value becomes larger than 6.1. Thus aniline is certainly more refractive than would be anticipated from the usual run of benzene compounds and compound ammonias. Carbon in such compounds as naphthalene or phenanthrene has a much higher refractive power, to which he had, some years ago, provisionally assigned the value of 8.8. It had been remarked that the ethylene bonds in open chain compounds ought to retard light differently from the double bonds in the aromatic series. This was not to be easily recognised in the refraction of A, but it was, undoubtedly, the case in the dispersion. Such considerations must have much weight in the discussion of the structure of carbon compounds exhibiting special properties.

Dr. PERKIN said, in reference to Dr. Armstrong's remarks on the very high values obtained for the refractive power of the carbonyl compounds of nickel and iron, it must be remembered that these compounds were examined in the pure condition, whereas all other determinations of the refractive power of nickel and iron were made with dissolved salts and do not necessarily give true values for these metals. In the case of zinc compounds he had found that the value of this metal in zinc ethyl was 15.9, whereas solutions of zinc salts gave only 9.8. Therefore it was not safe to infer that in the carbonyl compounds nickel and iron had the values they apparently possessed in salts. Through the kindness of Mr. Mond, he had had the opportunity of measuring the magnetic rotation of the nickel and iron carbonyl compounds, and had found that they gave very high rotations; but at present no other compounds of these metals had been examined.

As to the values given for the refraction of carbon and hydrogen being perfectly constant, even in saturated compounds this appears to be doubtful. Taking the case of ethylene oxide, they must be somewhat lower than usually given, and, in some of the amines, they appear to be higher; this is seen on comparing primary and tertiary amines, the refraction, but more especially the dispersion, increasing as we pass from the former to the latter. In the aromatic series this is very evident. Aniline itself has an abnormally high value, but, as methyl is introduced into this compound, the refraction increases with each methyl introduced much more than the change of composition requires, the increase for the first methyl being 8.36, and the change of dispersion no less than 1.37, and that for the second methyl 8.51, and of dispersion 1.22; whereas the calculated difference in each case is 7.6 only, and for the dispersion 0.34. Corresponding results are observed in reference to the magnetic rotation of all these compounds, though in a much more striking manner.

Dr. Armstrong had also made reference to the refractive power of two nitranilines; that these should be high is only consistent with their being derivatives of aniline. As to whether the difference of position of the NO_2 group would influence the refractive power of these substances in any marked degree, the data we have would be against such an assumption. Dr. Gladstone had measured several series of ortho-, meta-, and para-compounds at his request, and had found them to give nearly identical results.

Mr. MOND drew attention to the very different values deducible for nickel, the atomic refraction calculated from Kundt's observations with the metal being 6.12, while that calculated from the oxide is 9.82 (*cf.* Mond and Nasini, *Zeit. Phys. Chem.*, viii., 150).

Ethereal Salts of Glyceric Acid.

Inactive.

Ethereal salt.	Density, 15°/15°.	Difference.	Boiling-point.
Methyl	1.2814	0.0905	119—120° (14 m.m.)
Ethyl	1.1909		120—121° (14 m.m.)
Propyl (normal)	1.1453	0.0456	126—127° (14 m.m.)
Isobutyl	1.1024		128—130° (13 m.m.)

Ethereal salt.	Density, 15°/15°.	Difference.	Observed rotation in 198.4 m.m. tube, α.	Active. Specific rotation, [α] _D .	Molecular rotation. $\frac{M. [\alpha]_D}{100}$	Deduced specific rotation of glyceric acid (C ₃ H ₅ O ₄), [α] _D .	Boiling-point.
Methyl	1.2798	0.0877	-12.2°	-4.80°	-5.76°	-5.43°	120° (13 m.m.)
Ethyl	1.1921		-21.7	-9.18	-12.30	-11.60	—
Propyl (normal)	1.1448	0.0473	-29.4	-12.94	-19.15	-18.07	—
Isopropyl	1.1303	0.0293	-26.5	-11.82	-17.49	-16.50	114—116° (13 m.m.)
Butyl (normal)	1.1155	0.0252	-24.4	-11.02	-17.85	-16.84	131—139° (14 m.m.)
Isobutyl	1.1051		-31.2	-14.23	-23.05	-21.75	—
Butyl (secondary)	1.1052		-23.2	-10.58	-17.14	-16.17	123—126° (13.5 m.m.)

*126. "The Ethereal Salts of Glyceric Acid, Active and Inactive." By PERCY FRANKLAND, Ph.D., B.Sc., F.R.S., and JOHN MACGREGOR, M.A.

The accompanying table contains the names of the glycerates, inactive and laevorotatory, which the authors have prepared, together with their densities, observed specific and molecular rotations, as well as the specific rotation of glyceric acid as deduced from the rotations of the several salts.

The method of preparation adopted for the methylic, ethylic, normal propylic, and normal butylic glycerates consisted in heating glyceric acid (either inactive or active) with an excess of the particular alcohol in a sealed tube at about 180° C., and then fractioning the resulting products by distillation under greatly reduced pressure. In the case of the secondary alcohols, this method yielded an unsatisfactory result, and consequently the isopropylic and secondary butylic salts were prepared by saturating a mixture of glyceric acid and the alcohol in question with hydrogen chloride gas, and then fractioning under reduced pressure. This method was also adopted in the case of isobutylic glycerate, although this compound could also, doubtless, have been satisfactorily prepared by the sealed tube method. It was found that the facility of etherification was much greater in the case of the primary than in that of the secondary alcohols, whilst in the case of the tertiary butyl alcohol (the only tertiary alcohol experimented with) it was not found possible to obtain an ethereal salt.

In preparing the isopropylic and secondary butylic salts, a considerable quantity of a white substance was formed which was found to be an anhydride of glyceric acid, whilst in the attempt to prepare the tertiary butylic salts, this anhydride appeared to be the sole product.

The active ethylic glycerate was prepared by both the sealed tube and hydrogen chloride methods, and the resulting products were found to have the same rotatory power, thus showing that the activity is in no way impaired by the high temperature (180° C.) employed in the sealed tube method.

Attention is directed to the relationship between the molecular rotations of the several glyceric ethereal salts experimented with. This rotation increases almost quite regularly from methylic to ethylic, to normal propylic glycerate. Isopropylic glycerate has a somewhat lower rotation than the normal propylic compound, but the isobutylic glycerate lies much more nearly on the "main line" of molecular rotatory increase than either the normal or secondary butylic compounds, the rotations of which correspond closely with that of the isopropylic

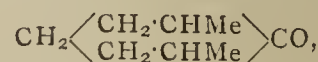
glycerate. It is pointed out that the addition of CH₂ to the alkyl group increases the molecular rotation by 6.54 in the case of methylic and ethylic, and of 6.85 in the case of the ethylic and normal propylic glycerates, whilst the increase is only 5.56 in the case of the isopropylic and isobutylic glycerates. These values for CH₂ are very similar to those which can be deduced in the case of ethereal salts of tartaric acid, in which, also, the rotatory value of CH₂ is less in the case of the iso than of the normal compounds.

In reviewing the rotatory power of these active glyceric ethereal salts in relation to the recently advanced theories of Guye and Crum Brown, they are of opinion that, although in the first three terms of the series, the increase in rotation follows the increase in the weighting of one of the groups attached to the asymmetric carbon atom, yet that by a consideration of the rotatory powers of the higher terms, as well as by a comparison of the rotations of ethylic glycerate and ethylic lactate (the only active lactic ethereal salt hitherto prepared), it is obvious that the molecular rotation is affected by the qualitative nature of the groups as well as by the relative magnitude of their masses.

127. "Formation of the Ketone 2:6-Dimethyl-1-ketohexaphane from Dimethylpimelic Acid." By F. STANLEY KIPPING, Ph.D., D.Sc.

In a recent paper by the author and Mackenzie (C. S. Trans., 1891, 569), it was stated that "when dimethylpimelic acid is heated with phosphoric anhydride at a moderately high temperature, it yields an oil having a strong turpentine-like odour; this reaction will be further investigated by one of us."

Although, on continuing the experiments, only a very small quantity of the oil was obtained in the manner indicated, owing to the formation of resinous products, the investigation was not relinquished, as it seemed probable that the product would prove to be a dimethylketohexamethylene (2:6-dimethyl-1-ketohexaphane, cf. Proc. C. S., 1892)—



the formation of which in this way would be of considerable interest, not only on account of the nature of the product, but also as showing that dicarboxylic acids are capable of undergoing a change similar to that already studied in the case of the fatty acids (Trans., 1890, 532, 980).

Ultimately, by distilling the calcium salt of dimethylpimelic acid with soda lime under reduced pressure, an

oil was obtained which, after agitation with soda solution, was distilled, and the portion boiling at about 180° collected separately; this fraction contained a *ketone* of the composition $C_8H_{14}O$ (found, $C=76.5$, $H=11.1$ per cent; calculated, $C=76.2$, $H=11.1$ per cent), capable of interacting with hydroxylamine, forming a *hydroxime* of the composition $C_8H_{14}:NOH$, crystallising from light petroleum in colourless prisms melting at about 112° ; the hydroxime had an odour very similar to that of camphor hydroxime.

The ketone is, in all probability, a dimethylketohexamethylene; it has a peppermint-like odour, which seems to be characteristic of the cyclic ketones of this class, ketopentamethylene (Wislicenus and Hentschel), methylketopentamethylene (Semmler, *Ber.*, xxv., 3517), and suberone, which is probably a methylketohexamethylene (compare Kipping and Perkin, *Trans.*, 1891, 217), being all described as having this particular odour.

The publication of this note at present time seems to be desirable in view of the fact that in the last number of the *Berichte* (p. 231) von Baeyer has described a ketone, obtained by the distillation of calcium pimelate with soda lime, which is doubtless a homologue of the compound prepared by the author. The investigation is being continued.

128. "Note on the Interactions of Alkali-metal Haloids and Lead Haloids and of Alkali-metal Haloids and Bismuth Haloids." By ELEANOR FIELD, Assistant Demonstrator in Chemistry, Newnham College, Cambridge.

By boiling potassium or ammonium iodide with lead iodide, chloride, bromide, or fluoride and water in the ratio of 30 parts of the former to 1 part of the lead compound to 75 parts of water, pale yellow needle-like crystals were obtained, having the composition $3PbI_2 \cdot 4KI$ or $3PbI_2 \cdot 4NH_4I$.

By boiling potassium or ammonium chloride, or bromide, with lead iodide and water in the ratio of 6 parts of the former to one part of the lead compound to 50 parts of water, lead iodochloride, $PbICl$, was obtained.

By boiling potassium or ammonium iodide with lead chloride and water, in the ratio of 1 part alkali of the former to 5 parts lead chloride to 250 parts water, iodochlorides of lead of the composition $PbI_2 \cdot 3PbCl_2$ and $PbI_2 \cdot 5PbCl_2$ were obtained; when lead bromide was used in place of lead iodide, the product was an iodobromide of lead, $PbI_2 \cdot 2PbBr_2$.

These results show that when a large excess of potassium or ammonium iodide is used, the whole of the lead haloid is transformed into iodide, if the lead compound was not iodide to start with, and that the lead iodide thus formed combines with the potassium or ammonium iodide to form a double salt; but that if less alkali-metal haloid be used in proportion to the amount of lead haloid employed, the product contains the halogen of the two haloids, and it is free from alkali-metal. The composition of the products of the interaction depends more on the relative quantities of the interacting haloids than on the nature of the metals and the halogens of the salts employed.

The results obtained by the interactions of the alkali-metal and bismuth haloids differed from those obtained with lead haloids. The compound $BiBrCl_4K_2$ was obtained by dissolving bismuth chloride in solution of potassium bromide used in the ratio $BiCl_3 : KBr$. The compound $BiClBr_4K_2$ was obtained when bismuth bromide was dissolved in solution of potassium chloride in the ratio $BiBr_3 : KCl$. But when bismuth chloride and ammonium bromide interacted in the ratio $BiCl_3 : NH_4Br$, the same substance was obtained as when bismuth bromide interacted with ammonium chloride in the ratio of equal numbers of molecules, viz., $BiCl_3Br_3(NH_4)_3$. This compound is similar to the $SbCl_3Br_3K_3$ obtained by Atkinson (*C. S. Trans.*, 1883, p. 289) by the interaction of antimony and potassium haloids, either in the ratio $SbCl_3 : 3KBr$ or in the ratio $SbBr_3 : 3KCl$.

These results indicate that the composition of the products of change is dependent, not only on the relative masses of the interacting haloids, but also on the nature and relative affinities of the halogens and also of the metals of the interacting haloids.

129. "An Isomeric Form of Benzylphenylbenzylthiourea." By AUGUSTUS E. DIXON, M.D.

Phenylthiocarbimide and dibenzylamine interact, forming the compound $C_6H_5N:C(SH) \cdot N(C_7H_7)_2$, isomeric with the thiourea $C_7H_7N:C(SH) \cdot NC_6H_5 \cdot C_7H_7$ (m. p. 103°), previously obtained by the author (*Trans.*, 1891, 567) from benzylthiocarbimide and benzylaniline: it crystallises in vitreous prisms, insoluble in water, rather sparingly soluble in ether and alcohol, and melting at $145-146^{\circ}$ (uncorr.); it is converted by the action of alcoholic ammonia at $100-110^{\circ}$ into phenylthiourea and dibenzylamine.

130. "A New Atomic Diagram and Periodic Table of the Elements." By R. M. DEELEY.

After a reference to Lothar Meyer's diagram of atomic volumes and Mendeleeff's periodic table of the elements, a diagram is described in which the ordinates are "volume heats" and "volume atoms" instead of atomic volumes; a table of the elements is also given, in which the elements are arranged periodically, in accordance with their positions on the diagram.

The volume heats are obtained by multiplying specific heat by relative density, and the volume atoms by dividing relative density by atomic weight.

Hofmann Memorial Lecture.

An Extra Meeting of the Society will be held on Friday, May 5th, 1893, the anniversary of the death of A. W. von Hofmann, when addresses will be delivered by the Right Hon. Lord Playfair, K.C.B., F.R.S., V.P.C.S.; Sir F. A. Abel, C.B., F.R.S., V.P.C.S.; Dr. W. H. Perkin, F.R.S., V.P.C.S.

Experimental Conclusions on the Use of Sand-Filters.—The result of deliberations carried on in the Imperial Sanitary Office (Kaiserliches Gesundheitsamt), in order to exclude as far as possible the danger of infection from the use of filtered river-water as a supply for towns, may be summed up as follows. Care must be taken that the water used as a supply (river, lake, &c.) must be as far as possible guarded against pollution by human excretions; the mooring of vessels near the spot whence the supply is taken must be especially prevented. A sand-filter does not yield a water absolutely free from germs, and as their efficacy in keeping back micro-organisms, including cholera germs, is limited, the demand made upon the filters must not be increased beyond a certain limit. The speed of filtration must not exceed 100 m.m. (?) hourly. In places where the consumption of water is so great that the above rate of filtration is exceeded remedial measures must be taken. This is effected either by a limitation of the consumption (for which purpose the introduction of water meters in each house is recommended), or by increasing the surface of the filters and installing additional filter-beds. Filters which have become clogged must be removed only so far that a stratum of sand remains of more than 40 c.m. in thickness. The water first run off from a newly built filter, or from one supplied with fresh sand, must not be allowed to flow into the clean water reservoirs or into the mains as it is rich in bacteria. The performance of the filters must be daily checked by bacteriological examination. If greater numbers or unusual species of microbia suddenly appear, the water must be shut off from use and precautions taken. It is even desirable to examine the filtrate from each filter separately. Careful attention to these directions reduces the danger of the entrance of cholera germs into the branch water to a minimum, as it has been lately shown on a large scale by the instance of Altona in comparison with Hamburg.—*Journal Gas-Beleuchtung and Chemiker Zeitung.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 11, March 13, 1893.

An Electric Furnace.—Henri Moissan and Jules Violle.—The arrangement of the furnace cannot be intelligibly described without the two accompanying figures.

Photographic Properties of the Cerium Salts.—M. Auguste and Louis Lumière.—This paper will be inserted in full.

Metallic Osmium.—A. Joly and M. Vèzes.—Already inserted.

Researches on Thallium: Re-determination of its Atomic Weight.—Charles Lepierre.

The Zinc and Cadmium Fluorides.—C. Poulenc.—This paper will appear *in extenso*.

Determination of Mercury in Dilute Solutions of Sublimate.—Leo Vignon.—The author takes, *e.g.*, 50 c.c. of a solution of mercuric chloride at one part in a thousand, adding 5 c.c. of pure hydrochloric acid at 22° and 10 c.c. of a clear saturated solution of hydrogen sulphide. The yellow precipitate obtained rapidly turns black; it is filtered through a filter, weighed to one-tenth m.grm., washed, dried, and pressed. It is useful to operate comparatively upon a check filter-paper, through which is filtered a mixture of 50 c.c. distilled water, 5 c.c. HCl, and 10 c.c. H₂Cl, which is washed like the former. The weight of this check filter, of the same size and the same paper as the filter containing the precipitate, gives a small corrective coefficient which permits the weight of the mercury sulphide to be determined with more accuracy. In solutions containing one part of mercuric chloride in 10,000, a gravimetric process cannot be applied with accuracy except we can operate upon at least 500 c.c. of solution.

Alkaline Polyphenolic Phenates.—M. de Forcrand.—A thermochemical paper which does not admit of useful abstraction.

Isomerism of the Amidobenzoic Acids.—Oechsner de Coninck.—The author finds that the *meta*-acid is the most soluble, that the *ortho*- and *para*-acids are less soluble, and in distilled water possess a solubility almost equal respectively.

The Action of Carbon Monoxide upon Reduced Hæmatine and upon Hæmochromogen.—H. Bertin-Sans and J. Moitessier.—The authors have obtained a compound of carbon monoxide with hæmatine by setting out directly from reduced hæmatine without having recourse to hæmochromogen.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. ix. and x., No. 5.

Dibromogallic Triacetic and Tribenzoylic Acids.—Alex. Bietrix.—The composition of these compounds is C₆Br₂(OC₂H₃O)₃COOH and C₆Br₂(OC₇H₅O)CO₂H.

Researches on the Constitution of the Colouring-Matters of the Rosaniline Group and their Acid Salts.—A. Rosenstiehl.—Already inserted.

Identity of the Hydrocarbide, C₇H₁₄, derived from Perseite or from Resin with Heptanaphthone (Methylcyclohexane).—L. Maquenne.—The author establishes the identity of the saturated hydrocarbide, C₇, of perseite, that of the essence of resin, that obtained by Markownikoff by saponifying the iodide of the alcohol corresponding to suberone, heptanaphthene, and finally Wreden's toluene hexahydride.

The Alizarin Formamides.—M. Prud'homme and C. Rabaut.—The two amidoalazarins are transformed into formamides under the action of formic acid.

An Electric Furnace.—M. Saladin.—This paper requires the accompanying figure.

Preparation of Amylpyrusate.—L. Simon.—The mixture, in theoretical quantities, of pure pyruvic anhydride and of amylic alcohol is kept for some hours at ebullition under a reduced pressure with an ascending condenser. The condenser is then replaced by a Le Bel apparatus with three bulbs, followed by a descending refrigerator, and distils slowly on the water-bath under a pressure of 10 to 15 m.m. There passes over first a little water and then amylic ether. The yield is theoretical.

A Reaction of Cupric Salts.—E. Lenoble.—If into the solution of a cupric salt we pour a solution of double mercury and potassium iodide, we obtain a fine bright red precipitate, whilst a certain quantity of iodine is set free and colours the liquid brown. The precipitate seems to be a compound of cuprous iodide and mercuric iodide.

Production of Mucic Acid (Hexabepic Acid) by the Oxidation of Gum-Arabic.—E. Maumené.—Not suitable for reaction.

On Guyacol.—A. Béhal and E. Choay.—The guyacols of commerce are essentially variable products, their boiling-points ranging from 200° to 215°. None of them contains more than 50 per cent of definite guyacol, the rest consisting chiefly of cresylol and cresol. Pure guyacol is a white, crystalline solid, fusible at 28.5° and boiling at 205.1°.

On Asboline (Pyrocatechine and Homopyrocatechine).—MM. Béhal and Desvignes.

Analysis of Official Creosotes.—A. Béhal and E. Choay.—These two papers are not suitable for abstraction.

Chemical Conditions of the Action of Diastase.—Dr. Jean Effront.—The author finds the nitrogenous residue from the manufacture of glucose, and studies the behaviour of its constituents with asparagine, aluminium, and phosphoric acid.

On Potassium and Ammonium Tetrachromates.—G. Wyruboff.—M. Schmidt's note in the *Berlin Berichte* has been anticipated by the author twelve years ago.

MEETINGS FOR THE WEEK.

FRIDAY, April 7th.—Geologists' Association, 8.
Quekett Club, 8.

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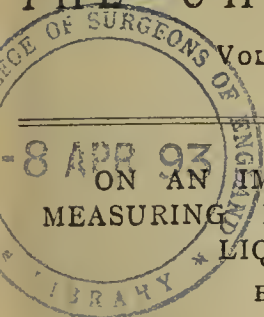
N. H. MARTIN, C. E. STUART, B.Sc., H. SPARGO, A.Sc., F.I.C.

ST. PAUL'S SCHOOL, West Kensington.

An Examination for filling up about three Vacancies on the Foundation will be held on the 12th April next.—For information apply to the Bursar, St. Paul's School, West Kensington.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1741.

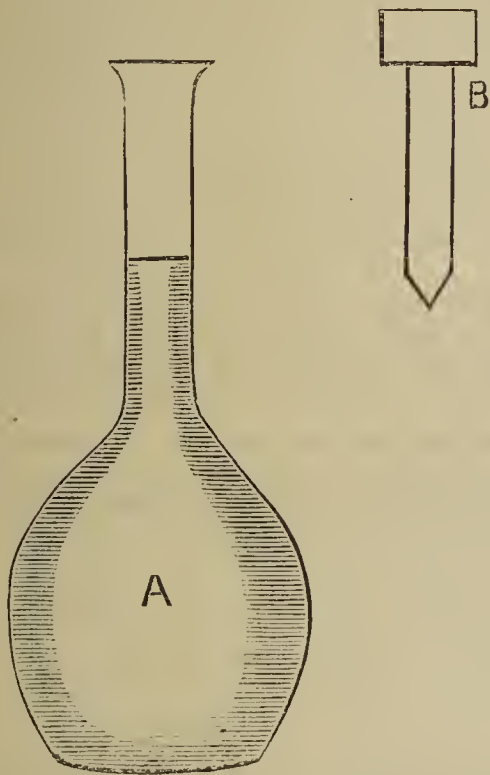


ON AN IMPROVED STOPPER OF
MEASURING FLASKS FOR MEASURING
LIQUIDS QUICKLY.

By ALEX F. REID.

DURING the last year I have had several articles in the CHEMICAL NEWS (vol. lxx., pp. 68, 125; vol. lxxi., p. 166) on improvements in analytical apparatus. These improvements were effected chiefly to save time in the analytical operations of the laboratory. They are in constant use, and by their means much more work is got through with quite as accurate results. I refer to their use in the laboratory of the Cassel Gold Extracting Company, Ltd., of Glasgow, for the testing of potassium cyanide.

There is still a simple contrivance which I find of much use in measuring out water in litre or other flasks. It consists of a wooden or indiarubber plug, B, which fits loosely into the neck of the flask, A, and of such a size



that the part of it that goes into the flask has the same volume as the part of the flask above the mark. The flask is first filled up past the graduation line with water. The stopper is inserted and then pulled out. The surplus water runs out, and the right quantity remains. The stopper has a tapered point to admit of its being put in quickly, and also to allow the water to run off readily when it is being withdrawn.

Bonshaw, Stewarton, N.B.

Royal Institution.—On Saturday, April 15, Mr. James Swinburne, M.Inst.E.E., will begin a course of three lectures on "Some Applications of Electricity to Chemistry." The Friday Evening Meetings will be resumed on April 14, when Sir William H. Flower will deliver a discourse on "Seals."

ON ZINC AND CADMIUM FLUORIDES.

By C. POULENC.

MARIGNAC has shown that zinc fluoride, $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$, loses its water at 100° and appears in the form of a white amorphous powder. We have succeeded in preparing it anhydrous and crystalline by applying the methods which we have formerly indicated.

1. *Action of Anhydrous Hydrofluoric Acid upon Zinc.*—Gaseous hydrofluoric acid does not attack zinc except above a dull red heat. Zinc fluoride is formed and hydrogen escapes. For the platinum tube we have hitherto made use of a tube of retort-coke to avoid the formation of an alloy of platinum and zinc.

2. *Action of Anhydrous Hydrofluoric Acid upon Melted Zinc Chloride.*—Melted zinc chloride is decomposed in the cold by vapours of hydrofluoric acid, but the temperature must be raised to 800° or 900° in order to obtain anhydrous crystalline zinc fluoride. Under such conditions we observe that the sides of the platinum tube are coated with fine colourless transparent needles of volatilised fluoride, and that the contents of the platinum boat likewise present the aspect of a crystalline mass.

3. *Action of Anhydrous Hydrofluoric Acid upon Zinc Oxide and Zinc Hydroxide.*—These two substances equally give rise to anhydrous crystalline zinc fluoride if heated below redness in a current of gaseous hydrofluoric acid.

Properties.—Zinc fluoride appears in the form of fine transparent colourless needles. They polarise light strongly, and belong apparently to the monoclinar or triclinar system. The specific gravity at 15° is 4.84. It is sparingly soluble in cold water, but its solubility increases with the temperature. It is insoluble in alcohol at 95° . Hydrochloric, nitric, and sulphuric acids dissolve it at the temperature of ebullition. Zinc fluoride is reduced at a red heat by hydrogen, which carries away vapours of zinc. If ignited in the air it is converted into zinc oxide. Watery vapour produces the same reaction at a red heat. Gaseous hydrogen sulphide passing over heated zinc fluoride decomposes it into zinc sulphide and hydrofluoric acid. Gaseous hydrochloric acid under the same conditions yields melted zinc chloride. If melted with alkaline carbonates there is formation of zinc oxide and an alkaline fluoride.

Cadmium Fluoride.—If we evaporate a hydrofluoric solution of cadmium fluoride we obtain, according to Berzelius, a crystalline fluoride, adhering very strongly to the sides of the vessel in which it has been formed. This compound, which we have dried in the stove at 120° , still retains a small quantity of water, and does not correspond to a well-defined formula. We have succeeded in preparing anhydrous cadmium fluoride by the same procedures which yielded zinc fluoride.

1. *Action of Anhydrous Hydrofluoric Acid upon Cadmium.*—Cadmium is attacked more readily than zinc and at a lower temperature. The experiments should be made in a tube of retort-coke to avoid the formation of metallic alloys.

Action of Anhydrous Hydrofluoric Acid upon Melted Cadmium Chloride.—Cadmium chloride, recently melted and pulverised, can scarcely be decomposed at the ordinary temperature by gaseous hydrofluoric acid. A rise of temperature facilitates the reaction, but never renders it complete. The cadmium fluoride formed remains in the boat as a colourless transparent melted mass, whilst the undecomposed cadmium chloride is volatilised.

Action of Anhydrous Hydrofluoric Acid upon Cadmium Oxide.—The acid decomposes it at a red heat, producing thus melted cadmium fluoride. But to whatever temperature we raise the fluoride (1200°) we never observe a trace of volatilisation. This latter character differentiates it distinctly from zinc fluoride.

The action of anhydrous hydrofluoric acid obtained by the moist way gives rise to the same compound as above.

Properties.—Cadmium fluoride, if it has been raised to a high temperature, is a colourless, translucent mass, which crumbles into small fragments with a conchoidal fracture. Its sp. gr. is 6.64. It is very soluble in water, but insoluble in alcohol at 95°. Hydrochloric, nitric, and sulphuric acids dissolve it at ebullition. The sulphuric solution, if evaporated on the sand-bath, deposits anhydrous crystalline cadmium sulphate. This compound, which the author believes he has been the first to make known, is formed of small, colourless, very brilliant prisms, which gradually tarnish on exposure to air.

Cadmium fluoride is reduced by hydrogen at redness. If ignited in the air it is totally converted into cadmium oxide. Watery vapour at red heat gives the same reaction.

Hydrogen sulphide, if passed over cadmium fluoride, slightly heated, decomposes it into yellow cadmium sulphide and hydrofluoric acid. Gaseous hydrochloric acid under the same conditions yields cadmium chloride. This reaction, which takes place more easily than the inverse reaction, explains why we have never obtained the complete conversion of cadmium chloride into fluoride.

Melted alkaline carbonates decompose it into cadmium oxide and an alkaline fluoride.—*Comptes Rendus*, cxvi., p. 581.

IN MEMORY OF C. W. SCHEELÉ.

ON December 9th last, the 150th anniversary of the birth of Scheele, A. E. von Nordenskiöld, the celebrated Polar explorer, published a collected edition of his correspondence and laboratory notes. From a notice of this work from the pen of E. von Meyer (*Journ. für Prakt. Chemie*) we make the following excerpts:—

"Although Scheele is sufficiently known as a promoter of analytical chemistry it was little imagined that he had in the acutest manner utilised his observations for the development of quantitative methods. We now learn that he was the first to carry out the separation of iron and manganese by means of acetic acid. He further made use of the alkalies for opening up silicates; he recognised the difference between soluble and insoluble silica, and in 1772 paved the way the discovery of which has been mistakenly credited to Bergman. With the reactions of the salts of magnesium, copper, and mercury he showed himself acquainted to an extent shared by none of his contemporaries. He was aware that silver chloride is soluble in hydrochloric acid but insoluble in nitric acid, and he utilised the flame colourations of the salts of potassium and sodium.

"He has hitherto been acknowledged along with Priestley as the discoverer of oxygen, though Priestley is said to have first observed the gas a year earlier than Scheele. But from his laboratory notes and correspondence it now appears with full certainty that Scheele had obtained oxygen by various methods, and had described it accurately in 1771 or in the beginning of 1772. He named it first "vitriolic air," subsequently "fire air" (*aer purus*, *aer vitalis*). He prepared it then from nitrates (saltpetre, magnesium nitrate), from manganese ore and arsenic acid or sulphuric acid, from mercuric oxide, silver carbonate (along with carbonic acid), and from gold oxide. This fundamental discovery, from which a new epoch in chemical science must be dated, slept for some years and was made public in 1774 by Priestley, though in a much less complete manner.

"From the new work we learn to recognise Scheele, even in his earlier years, as a master in the treatment of gases. We find that as far back as 1770 he recognised nitrogen, hydrogen sulphide, hydrogen chloride, ammonia, and nitric oxide as distinct gases, and studied their properties. He was the first observer of liquid hydrogen sulphide and of chamber crystals.

"In his works we repeatedly find startling communi-

cations on the different stages of oxidation of the metals, especially iron, copper, and mercury, which he, of course, sought to explain on the phlogistic hypothesis."

THE ABSORPTION OF FREE NITROGEN BY PLANTS.

(Concluded from p. 149).

THE concluding experiments of M. Boussingault, on which he relies for the refutation of his own former conclusions, were, as we have already stated, made under such conditions that correct results could not be expected. He effected his cultivations in closed globes of the capacity of 6 to 10 litres!

As M. Ville justifiably asked, what can be expected of plants under such conditions?

A still more unfortunate departure from the natural conditions of plant-life was the very limited quantity of the sand used as soil. M. Boussingault used only 60 or 120 grms. for each experiment, a quantity about sufficient to fill the shell of a nut; and in such tiny lots of soil he sowed peas and haricot beans. Now, if a plant is to flourish, its roots must find in the soil a space adequate to the development which it should take. This condition is systematically violated in M. Boussingault's experiments, made in the years 1851 and 1852.

Another objection is, that to this reduced quantity of sand M. Boussingault added, as an inorganic manure, from 1 grm. to 10 grms. of the ash of farmyard manure. As such ash contains about 50 per cent of alkaline salts, the proportion of alkali was excessive to such an extent as to be injurious to plant-life.

Finally, the seeds were sown at a wrong season of the year. Every farmer and every gardener knows that this is a most serious error. A plant cultivated at the wrong time never takes a complete or normal development. For instance, wheat sown in May or June yields merely a grassy tuft. Colza sown in April flowers immediately after germination. Hence it could only be expected that the results of the experiments would be negative—as it was actually the case. To argue from results obtained under such unnatural conditions to what takes place in normal growth is eminently unscientific.

How decidedly contradictory are the conclusions which M. Boussingault has maintained at different times we need merely refer to his memoirs published in the *Comptes Rendus*.

In 1838 (*Comptes Rendus*, vi., p. 129) he asserts that the nitrogen of the air is absorbed by plants, and a report drawn up by M. Dumas and read before the Academy of Sciences formally consecrated this declaration.

In 1854 he asserts precisely the contrary (*Comptes Rendus*, xxxviii., p. 580).

In 1854 he announces that plants flourish in a confined atmosphere as well as in the open air (*Comptes Rendus*, 1854, xxxix., p. 603).

In 1859 he demonstrates just the opposite, i.e., that vegetation is more flourishing in the open air than in a limited confined atmosphere (*Comptes Rendus*, 1857, vol. xlviii., pp. 310 and 312).

In 1855 he states that plants cultivated with an addition of saltpetre live only from the nitrogen of this salt, and do not derive any from the air (*Comptes Rendus*, 1855, xli., p. 485).

In 1859 he recognises that a plant cultivated with the aid of saltpetre derives nitrogen from the air (*Comptes Rendus*, 1859, xlviii., 312).

Lastly, in 1866 he does not deny, but he does not distinctly affirm; he recognises that in the open air plants cultivated in ignited sand absorb a little nitrogen supplied by the ammonia of the atmosphere (*Revue des Cours Scientifiques*, 1865—1866, sixth issue, p. 97).

It is superabundantly plain that this admission is quite inadequate. The nitrogen present in the atmosphere in the state of ammonia, if entirely absorbed, would fall far short of meeting the wants of vegetation. This fact is the reason why some additional source has been sought for. Hence, if plants cannot utilise the free nitrogen of the atmosphere, we must admit that there exists in the soil, in the water, or in the atmosphere some abundant source of nitrogen which escapes our analysis. It is surely less rational to admit the existence of such an unknown source than to recognise the absorption of free nitrogen by plants.

In answer to the question how is such free nitrogen absorbed? we have positive facts to advance. Since the researches of Boussingault were effected, it has been established that the small nodules which we find in such abundance on the roots of beans and other leguminous plants are in reality minute chemical laboratories, in which the fixation of the atmospheric nitrogen is effected. The agents there at work are certain microbia. This fact explains the fertilising action of crops of clover when ploughed into the soil, as M. Ville has so ably and thoroughly expounded in his treatise "The Perplexed Farmer" (Longmans and Co.), or in his larger work on "Artificial Manures."

But we now find that not alone leguminous plants, such as clover and peas, but other kinds of vegetation, though not provided with root nodules, are able to absorb and fix free nitrogen. This M. Ville has shown analytically. If experimental plants are cultivated under normal conditions, the crop is found to contain an excess of combined nitrogen over and above what can be derived from the soil,—including the manures,—from the ammonia and nitric oxide of the air, and from ammoniacal salts existing in solution in the water. The patience and perseverance with which M. Ville has insisted on these phenomena demand the fullest recognition.

THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Continued from p. 150.)

Phosphorus.—The methods generally employed for the determination of this element consist in the conversion of the phosphorus into phosphoric acid by means of an oxidising agent, usually nitric acid, and the subsequent precipitation either as ammonium magnesium phosphate or ammonium phospho-molybdate. Chemists differ considerably in opinion as to which of the methods is the better. We are of opinion that the last named, or the "molybdate" method, as it is termed, is preferable, and for this reason it will be the only one we shall describe. The process requires the employment of a solution of molybdate of ammonia, which is prepared by dissolving 60 grms. of the crystals in water, making up to a volume occupying a litre, and adding 50 c.c. of ammonia (sp. gr. 0.88), and a slight excess of ammonium nitrate. The solution is allowed to stand for two or three days, and is then decanted from any precipitate formed.

For the analysis 4 grms. of the sample (with very pure irons it is sometimes necessary to use as much as 10 grms.—with phosphoric irons 2 grms., or even 1 gm. is quite sufficient) are placed in a porcelain dish, covered with 60 c.c. of nitro-hydrochloric acid, and heated at a gentle temperature until the iron is dissolved. The resulting solution is now carefully evaporated to dryness and heated highly. This is continued until the whole residue becomes black. Upon cooling, the residue is moistened with 60 c.c. of hydrochloric acid, the solution heated and taken to dryness in order that complete

separation of the silica shall be ensured. The whole is then re-moistened with a small quantity of hydrochloric acid and heated until solution is effected. To the resulting liquid five times its volume of hot distilled water is added, and the silica separated by filtration. The filtrate contains the phosphoric acid, but before it can be precipitated a large portion of the hydrochloric acid must be got rid of, and the volume considerably lessened. This is effected by adding nitric acid (sp. gr. 1.42) and evaporating to a thick syrupy condition, which operation is repeated until it is judged from the colour of the solution (which becomes lighter as the quantity diminishes) that the greater portion of the hydrochloric acid has been expelled. Finally, to the syrupy mass sufficient nitric acid is added to cause it to flow freely in the precipitating vessel, and 50 c.c. of the ammonium molybdate solution is then added. The liquids are thoroughly assimilated by brisk agitation, and the vessel is set aside to stand for a few moments in a warm place. The next step is to ascertain, as far as can be judged by smell, whether the solution is of the right degree of acidity, so that while, on the one hand, there is sufficient acid present to prevent an excess of ammonium molybdate coming down along with the phosphorus, there is not, on the other hand, sufficient to prevent the complete precipitation of the phosphorus. If it is found that the solution is excessively acid, ammonia (sp. gr. 0.88) is cautiously added, the vessel agitated briskly to dissolve the precipitated iron, and allowed to stand for a few moments after each fresh addition, until only slightly so. We have ascertained that the molybdate precipitate is slightly soluble in dilute nitric acid. If the solution is ammoniacal, nitric acid (sp. gr. 1.42) is added until it is slightly acid.

(A solution of phosphate of iron was made, and mixed with excess of perchloride of iron. 100 c.c. of this solution contained 0.01152 gm. phosphorus. For the experiments 100 c.c. of the solution was poured into a tube 100 c.c. Burette divided into 200 parts, provided with an Erdman's float, so that the number of c.c. to be used could be accurately run out. *Expt. 1.*—To 25 c.c. solution excess of ammonia was added, then acidified with nitric acid, boiled, 8 c.c. molybdate solution added, and sufficient nitric acid until precipitation. Set aside on sand-bath 26 minutes. Mean of five trials, phosphorus found, 0.002868 gm.; phosphorus in solution, 0.002880 gm. *Expt. 2.*—25 c.c. solution as above was mixed with 12 c.c. molybdate solution, to ascertain whether excess of molybdate would interfere with the accuracy of the process. Phosphorus found, 0.003085 gm. *Expt. 3.*—10 c.c. molybdate solution added to 25 c.c. phosphorus solution afforded 0.002880 gm. phosphorus. *Expt. 4.*—16 c.c. molybdate solution added to 25 c.c. phosphorus solution, on four trials, afforded 0.003378 gm. phosphorus. *Expt. 5.*—12 c.c. molybdate solution added to 25 c.c. phosphorus solution, along with an excess of nitric acid, afforded 0.001369 gm. phosphorus. *Expt. 6.*—12 c.c. molybdate solution, added to 25 c.c. phosphorus solution, 7 c.c. excess of nitric acid. Phosphorus found, 0.00271 gm. *Expt. 7.*—As above, but 14 c.c. excess of nitric acid used. Phosphorus found, 0.001450 gm. (The experiments 6 and 7, when set aside for many hours, gave no further precipitate.) *Expt. 8.*—It was thought that in experiments 2 and 4, with 12 c.c. and 16 c.c. molybdate solution, a shorter time might suffice for the precipitation of the phosphorus. Accordingly, experiments 2 and 4 were repeated, but only allowed to stand 12 minutes. Phosphorus found, 0.002958 gm., experiment 2 (two trials) Experiment 4 repeated with 16 c.c. molybdate solution, and a slight excess of nitric acid for 12 minutes. Phosphorus found, 0.00295 gm. *Expt. 9.*—16 c.c. molybdate solution to 25 c.c. phosphorus; solution boiled, after precipitation of phosphorus set aside, for 15 minutes. Phosphorus found, 0.004254 gm. The foregoing experiments show that great caution must be exercised throughout the whole process.)

After the right degree of acidity is got, the solution is

* From *Industries*, February 4, 1893.

allowed to stand in a warm place until the yellow precipitate of phospho-molybdate has settled at the bottom of the containing vessel and the supernatant liquid has become clear. The precipitate is then collected on a tared Swedish filter-paper, a dilute solution of nitric acid of 1 acid to 10 water being employed to throw it on. The filter and contents should be washed six times with the dilute nitric acid solution, and then removed to a water-oven, dried, and re-weighed. The increase in weight is due, as is obvious, to phospho-molybdate, which contains 1.66 per cent of phosphorus.

Arsenic is precipitated as arsenic-ammonium-molybdate, by ammonium-molybdate, and, as the metal is sometimes present in iron and steel, a portion of it would be thrown down in conjunction with the phosphorus. This may be estimated by the known methods, or by the method of Stead. Arsenic may be eliminated by previous treatment with sulphuretted hydrogen.

Some chemists recommend, with a view of saving time, that the evaporation to dryness of the nitro-hydrochloric acid solution, as above described, be dispensed with, and that it be evaporated until it acquires a syrupy condition only, adding then simply hydrochloric acid, heating to boiling, filtering, &c., and determining the phosphorus in the filtrate as above. We have tried this method, which undoubtedly considerably shortens the operation, but we have always obtained lower percentages than those obtained by the method above described. The method is only applicable to steels containing little or no silicon. In pig-irons the silicon interferes with the accuracy of the results obtained by this method.

(To be continued).

TECHNICAL ESTIMATION OF MANGANESE IN ORES.

By ALBERT H. LOW.

PREPARE the following solutions:—A standardised solution of potassium permanganate, approximately one-tenth normal. A solution of oxalic acid containing about 11.46 grms. of $C_2O_4H_2 \cdot 2H_2O$ per litre. Determine the exact strength of this solution by titrating with the permanganate in the presence of hot dilute sulphuric acid in the usual manner, and then calculate its value in manganese on the basis that $C_2O_4H_2 \cdot 2H_2O = Mn$. It will be found 1 c.c. will equal about 0.005 grm. of Mn, or about 1 per cent when 0.5 grm. of ore is taken for analysis. A saturated solution of bromine in cold water. Always keep an excess of bromine in the bottle. Under the conditions to be described, 25 c.c. of this solution will precipitate about 35 per cent of manganese.

Method of Analysis.

Treat 0.5 grm. of the ore in a 16-ounce flask with whatever acids are necessary to decompose it. Usually 5 to 10 c.c. of hydrochloric acid or aqua regia are sufficient. Boil until the free acid is nearly gone. This may be accomplished in two or three minutes by manipulating the flask over a naked flame. Dilute with about 75 c.c. of hot water, and add an excess of ZnO. Boil to effect complete neutralisation of the acid. Now add an excess of the bromine solution (usually 25 c.c., never more than 50 c.c.), and boil for a minute or two until the excess is expelled, as indicated by the disappearance of the red fumes. An excess of ZnO should still be observed in the bottom of the flask. Filter, using a filter about 5 inches in diameter, and wash flask and precipitate several times with hot water. Place the washed precipitate, together with the filter, back in the flask, and add a sufficient amount, say 50 c.c., of dilute sulphuric acid (1 to 9). Run into this mixture, from a burette, what is judged to be an excess of the oxalic acid solution, re-

membering that 1 c.c. equals about 1 per cent of Mn. Heat the mixture to boiling, and then, if necessary, add more oxalic acid, so as to effect complete solution of the precipitate. Now dilute somewhat with hot water, and titrate the excess of oxalic acid with the permanganate solution. The number of c.c. of oxalic acid actually consumed by the MnO_2 is thus arrived at, from which the percentage of manganese is then calculated. The entire analysis need not occupy more than twenty minutes. None of the ordinary constituents of ores interfere with the method, and the results obtained are very satisfactory.

Of course other reducing agents can be used in place of the oxalic acid solution. When the latter is not at hand a weighed amount of the double sulphate of iron and ammonium will be found convenient.—*Journal of Analytical and Applied Chemistry*, vi., No. 12.

NOTE ON THE DETECTION OF CHLORINE, BROMINE, AND IODINE IN THE SAME MIXTURE.

By JOSEPH TORREY.

I READ Mr. Kebler's note on the above subject in the *Journal of Applied Chemistry* (October, 1892) with much interest. The problem is one of the most difficult in qualitative analysis. For an experienced chemist it is not so difficult, but the point is to find a method that can be used by students.

The object of this note is to describe some very slight modifications of Dr. Hart's method, which in my experience have made it a little more convenient. The general procedure was given by Mr. Kebler, and need not be repeated here. I have found no occasion to modify the details so far as the evolution successively of the chlorine, bromine, and iodine is concerned; but the bulb-tube arrangement figured in the original description, and the methods for detecting the halogens as they come off, have been modified as follows:—

Instead of the bulb apparatus originally described, I use a small tube having one small bulb blown on it, the tube being bent slightly away from the perpendicular about half an inch above where it leaves the cork. Above the bulb there should be about half an inch of tube left. The flask containing the mixture to be analysed is charged with ferric sulphate as usual, and the iodine evolved; a small piece of starch-paper is held in the steam as it emerges from the tube, and any iodine speedily shows itself. When the iodine has all been expelled by boiling, as will be seen by the negative indication of the starch-paper, a crystal of potassium permanganate is added, and, on heating, the bromine is evolved. For detecting it I use iodised starch-paper in the same way as starch-paper was previously used, and any bromine is easily detected. The boiling is continued until all bromine is gone, when the chlorine is detected as usual.

The only points where care is necessary in giving this process to students are the following:—

1. Care must be taken that very small quantities of substance are used. The merest trace of any one of the halogens will be detected with certainty, and large quantities only waste time and fill the laboratory with undesirable fumes.

2. The boiling must be continued till no trace of bromine can be detected before testing for chlorine. The boiling must be quite brisk, or bromine will be mechanically held back.

For delicacy, rapidity, and certainty I have yet to find the equal of this process. With a reasonable amount of care the character of the mixture is practically immaterial. In the original paper it appeared from the published

experiments (in which I suppose I had a hand) that a large quantity of bromine masked the iodine test. I have not found the same effect to be present when the starch-paper is used to detect the iodine.

During the last two years of the Summer School of Chemistry at Harvard University I have had many experiments made with mixtures of very varying proportions, and have never yet met with any but favourable and satisfactory results.

Last summer some work was done toward seeing whether the process could not be turned to account quantitatively. The outlook was encouraging, but the time was too short to accomplish enough to make it certain. I hope the work may be continued the coming summer.—*Journal of Analytical and Applied Chemistry*, vi., No. 12.

A NEW PROCESS FOR THE MANUFACTURE OF MANGANESE ON THE COMMERCIAL SCALE.*

By WM. H. GREENE and WM. H. WAHL.

WITHIN a few years manganese has assumed considerable importance as a constituent of several alloys, and the purest manganese of commerce as well as the richest ferro-manganese have been unsatisfactory for the preparation of these alloys by reason of the high proportion of carbon invariably present.

About two years ago we were induced to undertake the search of a process for the manufacture, on a commercial scale, of metallic manganese that would contain a minimum of detrimental impurities and be absolutely free from carbon. Before describing the process which we have elaborated, we will review briefly the history of the element.

About 1774, Scheele and Bergmann demonstrated that the metallic radical of manganese dioxide is different from iron, and John (Gehlen's *Jour. Chem. Phys.*, iii., 452) isolated the new element by heating a mixture of manganese carbonate and oil, powdering the resulting mass, again mixing it with oil, and strongly heating in a brasqued crucible.

St. Claire Deville (*Ann. de Chimie et de Physique* [3], xlvii., 182) modified this process as follows: he reduced pure artificially-prepared dioxide to red oxide; mixed this with sugar charcoal in insufficient quantity to reduce the entire quantity of oxide, and heated the mixture in a lime crucible to the highest temperature of a wind furnace.

Brunner (*Pogg. Annalen*, ci., 264) heated manganese fluoride, or a mixture of manganese chloride and calcium fluoride, with sodium in clay crucibles.

Giles (*Philosoph. Mag.* [4], xxiv., 328) prepared a manganese amalgam by the action of sodium amalgam on a concentrated solution of manganese chloride, and expelled the mercury by heating in a current of hydrogen, thereby obtaining pulverulent manganese.

Bunsen (*Pogg. Annalen*, xci., 619) obtained deposits of metallic manganese by electrolysis of a concentrated solution of manganous chloride.

The first attempt to produce the metal in considerable quantity appears to have been made by Hugo Tamm (*CHEM. NEWS*, xxvi., 111), who, in 1872, published the results of experiments made on certain modifications of John's method. Native dioxide was reduced by heating with powdered charcoal and oil in the presence of siliceous and fluorspar fluxes in graphite crucibles.

The problem presented to us was the reduction of a native oxide of manganese, for it is apparent that the expense of preparation of halogen compounds of the metal, and their subsequent reduction, would preclude

the possibility of applying such a method to manufacturing on a commercial scale.

At the outset of our work it became evident that the first step in the process would be the purification of the ore from iron, which would inevitably be reduced in the reduction of the manganese, and could not then be removed from the metal. Magnetic separation appeared to be the cheapest and most effective method, and we made exhaustive experiments in this direction, the ore being treated in all states of division and in all conditions of oxidation, between that of the natural ore and that in which the manganese was reduced to manganese monoxide and the iron to metallic iron. We were compelled to abandon the method entirely, because the iron and manganese are so intimately associated in the ore that no satisfactory separation can be accomplished by the magnet.

We then tried various electro-chemical methods, the ore being made the anode of baths containing sodium chloride solution, ferrous sulphate, dilute sulphuric acid, &c. By such means a certain proportion of the iron may be removed, but the separation is slow, and is far from complete when the manganese oxides begins to be attacked.

Convinced that only a chemical method would answer the purpose, we found after a number of experiments that nearly all the iron can be removed from rich manganese ores by digesting the pulverised ore with about 30 per cent sulphuric acid near the boiling point, while the manganese is practically unattacked. As an illustration of the effectiveness of the process, we may state that in a few hours the percentage of iron may thus be reduced from five or six to a few tenths, with a loss of not more than one per cent of the manganese present. The copperas that may be obtained by treatment of the waste acid with scrap iron will pay the cost of purification of the ore.

The reduction of the ore has been a perplexing problem. While it has never been denied that reduction by carbon in any form yields a metal containing a considerable proportion of the reducing agent, the literature of the subject indicated that this combined carbon might be removed by fusion of the metal under a layer of manganous carbonate or manganous oxide. Thus, Tamm (*CHEMICAL NEWS*, xxvi., p. 111) claims to have obtained from a pyrolusite containing 79.5 per cent Mn and 6.5 per cent F_2O_3 , a metal containing—

Mn	96.90
Fe	1.05
C	0.95
Other elements	1.10

and by refining this with manganese carbonate we have raised the proportion of manganese to 99.91 per cent. Other investigators admit the presence of more carbon in the product, but still claim that it may be removed by treatment with manganese carbonate. Our experiments show that the reduction by carbon takes place readily, and only after frequently repeated experiments, in which the proportions of oxide and carbon and the character and proportions of flux employed were varied through wide ranges, did we come to the conclusion that it is impossible by this method to prepare a metal containing less than about 6 per cent of carbon, and that it is equally impossible by fusion with an oxidising agent to remove carbon thus combined with manganese. The results of experiments recently published by Guntz (*Comptes Rendus*, cxiv., p. 115) explain clearly these phenomena. He finds that carbon monoxide is rapidly decomposed by manganese at a red heat, carbon and manganese monoxide being formed. It can then be readily understood why carbon free manganese cannot be made in the electrical furnaces nor in graphite crucibles.

From all these facts we have been led to infer that the reduction of manganous oxide by carbon yields not manganese, but a definite carbide having the composition

* Read before the Chemical Section of the Franklin Institute, March, 1893.

Mn₃C. We propose investigating this point in the future.

It then became evident that the problem could only be solved by a reduction taking place in the entire absence of carbon. Tentative experiments having given no encouragement to hope that an electrolytic method depending on the decomposition of fused baths of manganese chloride or manganese fluorides mixed with other chlorides and fluorides could be devised, the only alternative became a purely chemical process, the details of which were worked out during the progress of the laboratory work. The importance of these details will become apparent as we describe the steps of our process.

The pulverised manganese ore purified from iron, or containing less than one per cent iron, is exposed to the action of reducing gases at a temperature approximating redness. All the manganese is thus converted into greenish grey manganese monoxide, which must be allowed to cool out of contact with air to prevent oxidation to red manganosomanganic oxide.

The monoxide is then mixed with about 18 per cent of its weight of granulated aluminium and a suitable flux and the mixture is heated to a temperature near the melting point of cast iron in magnesite crucibles. The flux may be siliceous or a mixture of lime and fluorides, or lime alone. As soon as the temperature of reaction is attained the mass promptly fuses, and must be poured from the crucible while at its maximum temperature. While the character of the flux has little influence on the reaction, it has important relation to the yield and quality of the metal obtained. A siliceous flux naturally occasions the introduction into the manganese of a certain proportion of silicon. If the flux be too fusible a quantity of the aluminium may rise to the surface and escape the reaction. A mixture of lime and fluorspar has given us the best results in crucible operations.

Theoretically one part of aluminium should yield three parts of manganese; the best results we have obtained on the small scale, producing several pounds of manganese at one operation, have given us two and eight-tenths parts, or 93 per cent of the theoretical yield, and our average yield has been about 87 per cent. With aluminium at its present price we therefore estimate that the absolute cost of producing carbon free manganese containing, Mn 96 to 97 per cent, Fe and Si each one to two per cent, by our process, will be within thirty-five cents a pound, this estimate including all expenses.

On the large scale we purpose conducting the operation on a magnesite lined hearth, reducing gases being in slight excess. By this means we believe that the manganese will be retained in the state of lowest oxide until the temperature of reaction is reached, and that the prompt fusion of the flux at this stage will protect the manganese formed from contamination by carbon from the flame.

We may mention, in conclusion, that having experienced considerable difficulty in obtaining and preparing magnesite crucibles, we adopted the expedient of lining plumbago crucibles with a stiff paste of calcined magnesite. When properly prepared, these linings do not crack on drying, and do not shrink from the plumbago walls. After thorough drying, the crucibles are ready for use, and we have found the linings very serviceable, not only for the preparation of manganese, but in other metallurgical work in which siliceous or plumbago crucibles were from any cause objectionable.

On Solubilities.—A. Etard.—Gay-Lussac represented solubility at saturation graphically by plotting out the temperatures as abscissæ and the variable quantities of a salt which 100 parts of water can dissolve as ordinates. The author takes the ordinates as proportional not to the quantity of the salt dissolved by the fixed and arbitrary amount of 100 parts of water, but to the weight of the salt contained in 100 parts of the saturated solution.—*Bulletin de la Société Chimique de Paris*, No. 3.

GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Concluded from p. 152).

THE above report includes all the experiments that we made, whether successes or the reverse. On the other hand, we have to confess that the displacement of the reduction tube was not in all cases exactly equal to that of its tare. Originally this was the case to within less than 0.4 c.c., but the reduction tube had to be renewed twice, and the two new tubes were simply made on the model of the original one, and then weighed against the original tare without readjustment of the latter. Hence, before going any further, we had better calculate the maximum uncertainty which our oxygen weights are infected with on this account. The tare apparatus displaced 167.5 grms. of water, and as we took great care to make the new reduction tube as nearly as possible identical with the original one, it is almost impossible to assume that their outer volumes differed by more than, let us say, one-fifth of the value, or by 33.5 c.c. We will adopt this number as representing a limit-value for the unknown difference. Now, supposing the temperature and pressure of the atmosphere in the morning, when the first weighings were made, were t^0 and P' m.m., and the corresponding values at the second weighings were $t''=t'+\theta$ and $P''=P'+p$ m.m. (The latter values are given above, the former are before us in our Journal, but we do not deem it necessary to transcribe them here). Then we have for the greatest possible value of the error in a given experiment the approximate expression—

$$\pm 33.5 \times \delta \left(\frac{P}{P'} - \frac{\theta}{T} \right),$$

where δ stands for the weight of 1 c.c. of air in m.grms. as it was in the morning, and T for 273 + the temperature as it was in the evening. For the present purpose δ may be put down at the constant value of 1.227, and P at 760 m.m. We have calculated the corrections for the several experiments recorded, and found that the correction attains its maximum in the case of Experiment 5, for which it is -0.49 m.grm.; next after it comes Experiment 9 with -0.19 ; then Experiment 6 with -0.16 . For all the rest, the values found were considerably less. Hence this error may be neglected. In the following Table the first column gives the number of the experiment; the second, the values $h_0 : S_0$ found; the third, the value x calculated therefrom for the atomic weight of hydrogen; the fourth, as "residuals" the differences $x = x_0$, where x_0 is the adopted "mean value":—

Summary of Results.

No.	$h_0 : S_0$.	$x=8 (h_0 : S_0)$.	Residuals. $x_0=1.00913$.
6 0.125521	(1.00417)	-0.00496
10 0.125912	1.00730	-0.00183
12 0.125959	1.00768	-0.00145
9 0.126021	1.00817	-0.00096
3 0.126040	1.00832	-0.00081
7 0.126112	1.00890	-0.00023
8 0.126112	(1.00890)	-0.00023
2 0.126161	(1.00929)	+0.00016
14 0.126189	1.00951	+0.00038
11 0.126198	1.00959	+0.00046
1 0.126236	1.00989	+0.00076
13 0.126323	1.01059	+0.00146
5 0.126422	1.01138	+0.00225

Mean of the unbracketed

Nos. (10 experiments) 1.009133

$r \pm 0.00088, r_0 = \pm 0.00029$.

* *Proceedings of the Philosophical Society of Glasgow.*

The bracketed values, x , are excluded on account of the irregularities in the respective experiments, referred to in the context. For the remaining ten, the mean, the probable error, " r ," of a single experiment, and the probable error, " r_0 ," of the mean, are given at the foot of the Table. In accordance with the laws of probability, five of the residuals are less, and five are greater, than 0.00088. For a guess at the probable uncertainty of the mean result, let us take the mean of (1) the five lowest and (2) the five highest values of x , and divide the difference of the two means by 2. The former mean is 1.00807, the latter is 1.01019; half the difference of the two is 0.00106, or 3.6 times the probable error of the mean, which again falls in fairly well with the law of frequency of error.

Perhaps we had no right to exclude experiment No. 6. If we allow it to vote, the residuals and probable errors stand thus:—

No.	Residual = $x - 1.00868$.	
6	-0.00451	Mean = 1.00868
10	-0.00138	
9	-0.00051	
12	-0.00100	$r = \pm 0.00131$
3	-0.00036	$r_0 = \pm 0.00039$
7	+0.00022	
2	+0.00083	
14	+0.00091	
11	+0.00121	
1	+0.00191	
13	+0.00270	

Were we asked to name those of our experiments in which we have most confidence ourselves, we should select Nos. 7, 9, 10, 11, 12, 13, 14, because these proceeded with the highest degree of regularity. The mean of these seven experiments, the residuals, and the values, r , are as given in the following Table:—

No.	Residual = $x - 1.00882$.	
10	-0.00152	
12	-0.00114	
9	-0.00065	Mean = 1.00882
7	+0.00008	
14	+0.00069	$r = \pm 0.00079$
11	+0.00077	
13	+0.00177	$r_0 = \pm 0.00030$

Which of the three means shall we adopt? If there were any considerable difference between them, we should probably say "the mean of the eleven." But the deviations of the three results from one another are only slight, and for this reason we consider ourselves justified in adopting the mean of what we deem to be the seven best experiments as being in all probability the closest approximation to the truth. But, in any case, one correction still remains to be made; we refer to the occluded hydrogen in the metallic copper produced. In the course of our first series, we occasionally determined the occluded hydrogen quantitatively, and arrived at the conclusion that it might safely be neglected. This is still our opinion as far as that series is concerned, but the present, second, series affords a sufficient degree of constancy in the results to justify its application. Unfortunately, however, we arrived at this opinion only after all the work had been completed. The only thing we can do in the circumstances is to try and correct our present results by the occluded hydrogen determinations made in connection with the first series.

As a basis for our calculation, we will adopt four of the determinations quoted on page 105. For these, the uncorrected oxygen weights in grms., and the weights of water obtained from the occluded hydrogen in m.grms., were as follows:—

Page of Journal.	S.	Water from occluded hydrogen.
75	10.37	3.7
77	10.53	2.7
79	10.42	2.1
89	15.46	7.2
	46.78 grms.	15.7 m.grms.

Take ϵ as a symbol for the weight of occluded hydrogen per unit-weight of oxygen found, and adopting $O=16$ as the standard for atomic weights, the correction to be applied to the uncorrected value of H is -9ϵ . The value of 9ϵ , as calculated from the above numbers, is $=0.0003356$, hence we have for the corrected mean of—

	The 10 unbracketed experiments.	The same and No. 6.	The seven best experiments.
$H =$	1.00879	1.00834	1.00848

The fifth decimal, of course, if of no value whatever; we therefore adopt—

$H=1.0085$ ($O=16$), or $O=15.866$, or say 15.87 ($H=1$)

as the net result of our work.

The liquid water produced in the first, and also that produced in the second, series had been carefully collected and preserved in glass-stoppered bottles, and at the end of all the work we examined both for all the impurities that could reasonably be presumed to be present; but we obtained negative results in all cases. Very delicate litmus-paper remained unchanged, no sulphurous acid could be detected by permanganate, no nitrous acid by Griess's reagent, no ammonia by Nessler's, no metals by sulphuretted hydrogen. To test for nitric acid, 10 c.c. of each water were alkalisied by addition of a granule of carbonate of soda, and the solution was evaporated to about 0.5 c.c.; oil of vitriol was now added and ferrous sulphate poured on the top of the mixture as soon as it had cooled down sufficiently. There was no colouration even after long standing. To test for sulphuric acid, 5 c.c. of each of the waters was mixed with a drop of chloride of barium, and allowed to stand over night. No trace of a precipitate could be seen, even in the case of the water from the first series, which rather surprised us. We therefore tried to determine the least quantity of SO_3 , which the test would have revealed. A standard sulphuric acid, containing 40 grms. of SO_3 per litre, was diluted with water to 10,000 times its volume, and 5 c.c. of the dilute liquid, containing 0.02 m.grm. of SO_3 , tested with chloride of barium. After ten minutes a distinct opalescence was seen, but this did not increase on standing, and we felt convinced that an appreciably less quantity could not have been detected. To this extent, therefore, our water from the first series may be contaminated with sulphuric acid.

Being well aware that ours is not by any means the first attempt since the days of Erdmann and Marchand, to fix, as far as possible, the ratio $H:O$, we will now proceed to a brief review of the results of our predecessors.

STAS (Aronstein's translation of his memoir, pp. 57 and 58).—As the mean of nine experiments which agree almost absolutely with one another, Stas finds that 1 gm. of silver precipitates 0.49597 gm. of sal-ammoniac. Hence taking $Ag = 107.93$, $Cl = 35.454$, and $N = 14.046$, we have $NH_4Cl = 53.530$, whence $NH_4 = 18.076$, and $H=1.0075$, which number, considering that it is burdened with the errors of four experimentally determined constants, agrees wonderfully well with our own. But after all, even Stas's atomic weights cannot be presumed to be free of error, and we need only assume that while his NH_4Cl is by 0.01 too high, his Cl and N are each by 0.01 too low, to bring his value for $4 \times H$ down to 4 exactly. So the agreement, perhaps, is only accidental.

COOKE and RICHARDS (*American Chemical Journal*, vol. x., pp. 81—110, 191—196).—Abstract *Chemical*

Society's Journal, "Abstracts," year 1888, p. 547; and *Ibid.*, 910. C. and R. weighed their hydrogen directly in the Regnault fashion; but it is questionable if they gained much by doing so. Even if the hydrogen is absolutely pure, it is questionable whether the weighing of it, as a voluminous gas, affords a higher degree of exactitude than the indirect mode of taking the difference between the weight of the water and the weight of the oxygen, and, if it is contaminated with nitrogen, the indirect method is positively the more exact of the two. C. and R.'s hydrogen, it appears, was dried with oil of vitriol and phosphoric anhydride used together; hence their gas was probably contaminated with sulphurous acid. In their original determinations, they also neglected to allow for the expansion which their hydrogen-globe suffered, when, after having been tared (against a tare-flask of constant displacement) in an exhausted condition, it was filled with hydrogen of the pressure of the atmosphere. After this oversight had been pointed out to them by Lord Rayleigh, they corrected their original results, and found, finally, $H = 1.00825$, which, as we see, comes close to our own number.

W. A. NOYES (*American Chemical Journal*, vol. xi., pp. 155—161; abstract in the *Berichte der Deutschen Chemischen Ges.; Referate*, year 1889, p. 475).—An apparatus constructed entirely of glass in such a manner that the oxide of copper can be reduced, and the water weighed, within it, is (1) evacuated and weighed. It is then made to communicate with a source of pure hydrogen, the oxide of copper heated, and the water made to condense in the part provided for the purpose, care being taken to keep the oxide of copper slightly in excess. The apparatus is then closed, and weighed. (2) The water is removed by heating the apparatus and sucking out the vapour of water by means of a mercurial air pump. This being accomplished, the apparatus is weighed a third time. Taking W' , W'' , and W''' as representing the three weights, we have, for the hydrogen used, $W'' - W'$; and for the water formed $W''' - W''$. Six determinations gave (for $H = 1$), $O = 15.905$ to 15.876 ; mean $= 15.886 \pm 0.0028$. Or, for $O = 16$, $H = 1.00717$.

LORD RAYLEIGH (*Proceedings Royal Society*, vol. xlv., p. 425).—Two glass globes, of about 1800 c.c. capacity each, are charged, one with hydrogen, and the other with oxygen, of about one atmosphere's pressure, and they are then tared, each against a tare globe of exactly the same displacement. Suitable quantities of the two gases are then extracted by means of a mercurial air-pump (about 0.1 gm. of hydrogen and a slight excess of oxygen), and mixed together in a mercurial gas holder. The large volume of fulminating gas thus produced is exploded, in instalments, in the same eudiometer, and, in the ultimate residue obtained, the oxygen is determined volumetrically, to be reduced to weight by calculation. The weights of oxygen and hydrogen extracted from the globes are determined by weighing the globes after extraction of the gases, the shrinkage owing to the diminution suffered by the internal pressure being allowed for. In this manner all the data for calculating the ratio $O : H$ are procured. Five experiments gave for its value 15.92 to 15.98 , without allowing for shrinkage. The correction for it lowers the mean (15.95) by four parts in a thousand, and brings it down to 15.89 , corresponding to $H = 1.00692$, for $O = 16$. In connection with research by Rayleigh, it is important to notice that he used no oil of vitriol, but only fused caustic potash combinedly with phosphoric anhydride for drying his hydrogen, and took all imaginable precautions for avoiding contamination of his gas with atmospheric air.

Last, not least, we come to that admirable research which E. H. Keiser published in the *American Chemical Journal*, vol. x., pp. 249—261.* Of all the methods used

so far for the determination of the gravimetric composition of water, Keiser's impresses me as being the one which offers the surest guarantee for a correct result. Keiser's great hit is that he converts his hydrogen into hydride of palladium and weighs it in this compact form. The condensed hydrogen is re-expelled by heat, burned with oxide of copper, and the water collected and weighed, the displaced air being, of course, allowed for. The palladium (which, in Keiser's case, amounted to about 150 grms.) is contained in a glass tube provided with a soldered-on glass stopcock, constructed like the one characteristic of Lunge's nitrometer, so that we can either send off the liberated hydrogen by the horizontal boring or shut off the palladium-tube, and sweep the rest of the apparatus with a current of nitrogen or oxygen. The first step is to heat the palladium *in vacuo* to 250° for about 15 minutes. The palladium-tube is then made to communicate with an apparatus discharging hydrogen purified; finally, by means of a column of red-hot metallic copper, followed by an U-tube charged with phosphoric anhydride. The hydrogen proper combines with the palladium, the traces of nitrogen with which the gas was contaminated remain outside the palladium, and are removed by means of the air-pump. The exhausted tube is weighed against a tare-tube of the same displacement. It is then connected with the oxide of copper tube, the latter heated to redness, and the apparatus next filled with nitrogen to preclude the possibility of an explosion. After this preliminary operation the hydrogen is being gradually liberated, and converted into water. When the hydrogen is expelled as far as necessary, the palladium-tube is again shut off, and the hydrogen, which stagnates in the rest of the apparatus, swept out by means of a current of nitrogen. At the end the oxygen is turned on and kept going until the reduced copper is completely re-oxidised and its occluded hydrogen recovered as water. Ten experiments gave for the ratio $O : H$ values varying from 15.943 to 15.958 ; mean $= 15.9492$, or, for $O = 16$, $H = 1.00318$, which is by 0.00529 less than our own adopted value! I have tried hard to explain this not inconsiderable difference, and at last come to conceive the following hypothesis, which I give for what it may be worth. Keiser informs us that he *purified* his nitrogen by passing it successively over oil of vitriol, red-hot metallic copper, and phosphoric anhydride; but he does not tell us how he prepared it. There can, however, be little doubt that he prepared it as other people would have done, namely, by passing a current of purified air over red-hot copper previously reduced in hydrogen. That a man like Keiser should have forgotten to clear out all the *free* hydrogen left in his copper tube before using it for de-oxygenating his air, is not to be presumed, but in whatever way he may have done this, the reduced metallic copper was bound to contain occluded hydrogen, and it is not absurd to presume that this occluded hydrogen *did not all assume the form of water* when the air passed over it at a red heat. His nitrogen, as it came out of the gasholder, may have been contaminated with a trace of hydrogen, and, as a necessary consequence, his number for the weight of water corresponding to two parts of hydrogen may be too high. Supposing, for a moment, that Dittmar and Henderson's value for $O : H$ is the true value, then the 58.86263 grms. of water which Keiser produced in his ten syntheses (out of 6.5588 grms. of palladium hydrogen), included 0.2742 gm. of water from out of the hydrogen of his nitrogen gas; or, in other words, Keiser produced 27.4 m.grms. of adventitious water per synthesis, because the nitrogen gas he used contained, say, 3 m.grms. $=$ about 0.03 litre of hydrogen.

* At the time when we started our investigation, Keiser's experiments were known to me only by his preliminary notice in the *Ber. der Deutschen Chem. Ges.*, in which he gives three determinations of the ratio $O : H$, the mean of which is 15.872 . My impression at the

time was, that in all probability, Keiser's palladium hydride contained water, which, by being weighed as hydrogen, made his value for $O : H$ too low. His full memoir I saw for the first time when engaged in the compilation of this paper. If it had come to me in time, the present research would perhaps never have lost its original, purely critical character.—W. D.

I find it difficult myself to believe that it contained so much. Besides, my hypothesis cuts two ways. If nitrogen produced from reduced copper and air is liable to be contaminated with hydrogen, then our own determinations of the occluded hydrogen in certain of the lots of reduced copper which we produced in our first series falls short of the truth; and if they do, our " $H = 1.0085$ " is liable to a negative correction. Being an incorrigible "Proutian," I do not give up the hope that the true number may be 1.0000 after all.

To sum up, the weight of hydrogen which unites with 8 grms. of oxygen into water is, according to—

Dumas's experiments, as corrected by us—

(a) Assuming his water-weights are the true weights 0.989

(b) Assuming that he forgot to reduce his water-weights to the vacuum .. 1.0002

Erdmann and Marchand's, as corrected by us 1.006

(These three numbers, of course, are mere guesses, and must be taken for what they are worth).

Stas 1.0075

Cooke and Richards 1.0083

W. A. Noyes 1.0072

Lord Rayleigh 1.0069

Dittmar and Henderson, the seven best experiments 1.0085

These five independent investigations might be said to settle the question as far as it is possible in the present state of quantitative chemistry to settle it at all, if it were not for—

E. H. Keiser, who finds 1.0032

and it is impossible to pass over *his* research!

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 24th, 1893.

Prof. A. W. RÜCKER, F.R.S., President, in the Chair.

SEVERAL excellent photographs of flying bullets and of the air waves produced by vibrating hammers were exhibited, the originals of which had been taken by Prof. Mach.

A paper on "*The Differential Equation of Electric Flow*" was read by Mr. T. H. BLAKESLEY, M.A.

The object of the paper is to show that the ordinary mathematical expressions for electric flow fail to explain all known facts, and to point out that in order to interpret these facts certain properties of matter not usually recognised must be admitted. The subject is treated both algebraically and geometrically; in the latter case the magnitudes being represented by the projections of the sides of a triangle revolving in its own plane on a fixed line in that plane. Taking the ordinary differential equation for a simple circuit having resistance and self-induction, viz. :—

$$V - L \frac{dC}{dt} = RC,$$

it is shown that this takes no account of any energy except that spent in heating the conductor, and that where radiation into space is concerned, it is necessary to introduce another term, λC , where λ is a quantity of the nature of resistance. It is further pointed out that if work be done outside the circuit, the line which geometrically represents the induced E.M.F. cannot be perpendicular to that indicating the current and "effective" E.M.F., the latter term being defined to mean the

value of the quantity which is numerically equal to the product of the current into the resistance. A magnetic phase-lag must therefore exist. The author also shows that a magnetic field induced in phase with the magnetic induction would not result in a loss of energy, and no hysteresis could exist. Under the same circumstances there could be no radiation of energy from an alternating magnet.

A Leyden jar discharging through a circuit having self induction is next considered. Taking the ordinary premises, it is shown that no provision is there made for energy radiated into space, and that magnetic lag is necessary for the existence of such phenomena. The differential equations for the variables in condenser discharges, according to ordinary assumptions, are shown to be of the same form, and the variables can be represented by the projection of the sides of a triangle, which is simultaneously undergoing uniform rotation and linear logarithmic shrinking. The rate of shrinking is the same as that of the radius vector of an equiangular spiral of characteristic angle β , where—

$$\cos \beta = \sqrt{\frac{K}{L} + \frac{R}{2}};$$

K, L, and R representing capacity, self-induction, and resistance, respectively. The equations and their consequences are considered at some length, and several important properties brought out.

To allow for radiated energy, R must be virtually increased from R to $R + \lambda$, and the total energy is divided between the circuit and the field in the ratio of R to λ . If, therefore, the circumstances be such that λ is large compared with R, say by having high frequency, the heating of the circuit may only be a small part of the total energy. In this direction the author thinks the true explanation of some of Tesla's experiments is to be found, the energy being expended chiefly in radiation and not in current through the experimenter's body. When obtaining photographs of rapidly moving objects, Prof. Boys had used discharges of high frequency, but since several sparks of nearly equal intensity were obtained, the decay of amplitude was not very rapid, and the angle β of the logarithmic spiral representing the magnitudes would be nearly 90° . For the most rapid discharge $\beta = 45^\circ$, and the ratio of successive maxima was $e^{\pi} : 1$, i.e., 23.14 to 1 .

Prof. PERRY thought the C^2R term would not represent the heating of the wire when the oscillations were rapid, owing to the distribution of current not being uniform over the section of the conductor. Maxwell had shown that certain throttling terms had to be considered. In condenser discharges the complete equation would have many terms.

Prof. O. J. LODGE said the best definition of R in such cases was that derived from Joule's law rather than that of Ohm. Frequency was very important in the radiation of energy, but even at ordinary frequencies of alternators some energy was radiated. Referring to Tesla's experiments, he said the reason why no serious consequences followed was that there was not much energy behind them. High frequency might be instrumental in preventing injury, but this he thought remained to be proved.

Dr. SUMPNER pointed out that losses other than C^2R (R being the ordinary resistance of the conductor) had to be taken into account. In some cases, such as transformers on open circuit, the effective resistance might be one thousand times that of the coil. To discuss completely the problem taken up by Mr. Blakesley, it would be necessary to take account of non-uniform distribution of current both across and along the conductor, as well as the character of the magnetic and electric fields surrounding the circuit.

Mr. SWINBURNE thought there was a tendency to over estimate the rate of high-frequency currents, for unless the coils of transformers were assumed geometrically coincident, calculations were difficult. Errors of hundreds

per cent were quite possible. In Tesla's experiments no great power was involved, for the transformer could not give out any large power.

Mr. BLAKESLEY, in reply, said the term R was such that C^2R represented the whole waste in the conductor, whilst λ included everything wasted outside the conductor.

A paper on "*The Viscosity of Liquids*," by Prof. J. PERRY, F.R.S., assisted by J. GRAHAM, B.A., and C. W. HEATH, was read by Prof. PERRY.

The viscosity was tested by suspending a hollow cylinder within an annular trough containing the liquid and measuring the torque exerted on the cylinder when the trough rotated at various speeds about its axis. In the paper the equation of motion under the conditions of the experiment is discussed, the error introduced by assuming that the liquid moves in plane layers being shown to be about 0.5 per cent. To determine the torsional constant of the suspending wire, two methods were employed; in one, the turning moment required to produce a given angular movement was measured directly, and in the other, the torsional constant was determined from the period of oscillation. By measuring the viscous torques exerted with different depths of liquid in the trough, the correction for the edge of the suspended cylinder was found to be 0.8 c.m. On plotting the results obtained with sperm-oil at different temperatures and constant speed, a discontinuity was noticed about 40°. For a speed of 9 revs. a minute, the viscosity (μ) could be very approximately calculated from the formula $\mu = 2.06(\theta - 4.2)^{-0.686}$ below 40° C., and—

$$\mu = 21.67(\theta - 4.2)^{-1.349}$$

above 40° C., θ being the temperature. Experiments on the change of density of sperm-oil with temperature, made by Mr. J. B. Knight, indicated a minimum density about 40°. Subsequent experiments with other samples had not confirmed these observations. The paper contains several tables of the results obtained in various experiments. Those performed at constant temperatures show that for slow speeds the torque is strictly proportional to speed, but afterwards increases more rapidly, probably owing to the critical speed having been exceeded. The authors had also attempted to determine the viscosity from the damping of the torsional vibrations of the suspended cylinder, but the mathematical difficulties were found to be considerable.

After concluding the paper, Prof. PERRY read a letter he had received from Prof. Osborne Reynolds on the subject, who doubted whether the true critical velocities had been reached in the experiments. In the particular arrangement employed, he would expect no critical velocity in the outer ring of liquid, whilst in the inner ring the motion would be unstable from the first.

Prof. LODGE said he had tried whether the refraction or the density of sperm oil exhibited a discontinuity about 40°, but found none.

Mr. ROGERS pointed out that experiments which corroborated those of Prof. Perry had been made by M. Couette, and published in *Ann. de Chim. et de Phys.* [6], xxi.

Mr. E. W. SMITH suggested that the apparent discontinuity might be due to the separation of the constituents of an impure oil at certain temperatures and speeds of revolution.

Preservation of Constant Temperatures above the Boiling-Point of Water.—K. Ulsch (*Zeit. f. Brauwesen*).—The author connects a closed water-bath, by means of a flexible tube, with the upper end of a glass cylinder containing water and below it mercury. The pressure on the surface of the water forces the mercury into an ascending tube expanded above to a ball. Into the tube there opens a glass tube, cut off obliquely below, and leading to a burner below the water-bath. Gas is supplied by a tube opening laterally into the ball. The apparatus acts like an ordinary thermo-regulator.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. ix. and x., No. 2.

Polimarimetic Examination of Gums.—M. Guichard.—On examining the rotatory powers of gums they are found to form three series: those of Galam, Mogador, and Australia have a rotatory power near 16. Gums Arabic, Aden, and Amrad border upon 32, whilst gum Gatti has a rotatory power close upon 64. The facts may be explained by the view that the gums are mixtures of several dextro-rotatory and lævo rotatory substances.

On the Spontaneous Inversion of Cane-Sugar in an Aqueous Solution, and on the Cause of this Inversion, apparently Spontaneous, under the Influence of Light.—A. Béchamp.—The hypothesis of the inversion of cane-sugar by water alone in the cold must be rejected, and when it is apparently produced spontaneously the cause must be sought in the microzyme or a mould.

Action of Phenylhydrazine upon Camphoric Anhydride and the Camphoric Ethers.—C. Friedel and A. Combes.—The formula proposed by one of the authors to represent camphoric acid leads us to admit a ketonic function in the molecule of this acid, and of its anhydride. In the present paper they seek to demonstrate the existence of this function.

Sulpho-conjugated Compounds of Camphor and their Derivatives, Propyl-nitrophenol and Propyl-amidophenol.—P. Cazeneuve.—The acetylic derivatives with which the author chiefly concerns himself absolutely confirm the nature of the propylamidophenol, whilst its other properties and its mode of production confirm the constitution assigned to it by the author.

Constitution of Camphor.—P. Cazeneuve.—In consequence of facts recently discovered, we are more than ever authorised in declaring that an array of imposing facts gives a powerful support to the theoretic conception of Kekulé, which must remain founded in its essential features.

Facts Serving for the History of Gum Arabic.—A. Béchamp.—The author's experiments necessitate the conclusion that gum arabic contains a zymase which transforms amylaceous matter.

General Theory of Chemical Action.—E. Maumené.—The author claims the priority as against M. Raoul Piçet of the ascription to gravitation of a great part in chemical phenomena.

No. 3.

On Calcium Tartrate Extracted from the Dregs of Distilleries, its Determination and its Refining.—Ch. Ordonneau.—Already inserted.

The Rotatory Power of Grape-Must in Algeria.—H. and A. Malbot.—The rotatory power is very variable according to the ripeness of the grapes, the topographic position of the soil, and the nature of the cultivation. The alcoholic standard increases much more rapidly as the lævorotatory power decreases. It seems to the author that between saccharose and invert sugar there exists normally in grapes, at least in warm climates, a lævo-rotatory compound which differs from saccharose by its greater resistance to inversion.

New Method for the Determination of Fluorine.—A. Carnot.—This paper requires the three accompanying figures.

The Formula of Ordinary Tartaric Acid.—Albert Colson.—(A reply to MM. Friedel and Le Bel).—The

author shows that the stereochemical theories are neither simple nor clear, and that the notion of the product of dissymmetry based upon these theories is found once more in fault. It sins either in itself or in its foundations.

Action of Alkaline Alcoholates upon Camphoric Anhydride and other Anhydrides; Formation of Camphoric Ortho-Ethers.—P. Cazeneuve.—As the allo-ethers are still less easily saponifiable (Friedel) than the ortho-ethers, it appears that the analogies of camphoric acid with the succinic and phthalic acids are so remote that, like Friedel, we may search for novel interpretations.

On New Explosives.—A. Berg and L. C. Mautrand.—The hypophosphites mixed with chlorates form interesting explosives which seem to admit of applications. One mixture mentioned consists of equal parts of barium hypophosphite and potassium chlorate dried and powdered separately. If ignited in a confined place it has a shattering effect like that of mercury fulminate. It may be detonated by a slight shock or by the electric spark. Mixed with an equal quantity of magnesium powder it may be used for photographic purposes. Another mixture is that of sodium thiosulphate in a syrupy solution and powdered sodium chlorate. A drop heated on thin tinsel liquefies, boils up, dries, and gives an explosion like that of nitroglycerin.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 84.

Animal Charcoal.—Fiquier, a pharmacist of Montpellier, discovered the absorbent properties of animal charcoal in 1811. Devosne used it in 1812 to purify the juice of beets. Its regeneration was first attempted by Dumont in 1828. In Austria the manufacturers of sugar use their bone-black in large fragments up to the size of a walnut and wish for a porous product. In Germany the grains of the black must not exceed the size of a filbert, and must be as hard and compact as possible. The proportion of carbon must be 8 per cent, and the moisture must not exceed 8 per cent. In France the animal charcoal is required in grains varying from the size of linseed up to that of a filbert. Certain consumers demand at least 10 per cent of carbon and at most 6 per cent of moisture. In England and America the product is consumed almost exclusively of the size of millet-seed, as hard and as spherical as possible. The bones before carbonising are treated with light hydrocarbons of petroleum to remove the grease. The residue is dried at 70°, broken up into fragments, and charred in retort furnaces. The volatile oil given off (Dippel's oil) serves for denaturising alcohol. The thickness of the mass in the retorts should not exceed 20 c.m. The decolourising action of animal charcoal is explained by F. Schiller on purely physical principles, whilst Birnbaum and Bomasch recognise a chemical action.

MEETINGS FOR THE WEEK.

MONDAY, 10th.—Medical, 8.30.
TUESDAY, 11th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
— Royal Institution, 3. "Symbolism in Ceremonies, Customs, and Art," by John Macdonell, LL.D.
WEDNESDAY, 12th.—Geological, 8.
— Pharmaceutical, 8.
THURSDAY, 13th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, F.R.S.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
FRIDAY, 14th.—Royal Institution, 9. "Seals," by Sir William H. Flower, F.R.S.
— Astronomical, 8.
SATURDAY, 15th.—Royal Institution, 3. "Some Applications of Electricity to Chemistry," by James Swinburne, M.Inst.E.E. (The Tyndall Lectures).

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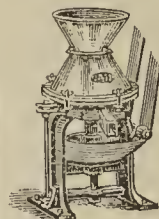
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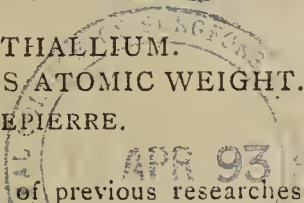
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THE CHEMICAL NEWS.

VOL. LXVII., No. 1742.



RESEARCHES ON THALLIUM.

RE-DETERMINATION OF ITS ATOMIC WEIGHT.

By M. CHARLES LEPIERRE.

I HAVE been led, in consequence of previous researches undertaken in concert with M. Lachaud (*Comptes Rendus*, 1891, July 27th), to undertake a re-determination of the atomic weight of thallium. The data furnished by different chemists vary in fact from 203.5 to 204.8, and the determinations have always been effected on thallous salts. In these experiments I have used the pure crystalline thallic oxide, Tl_2O_3 , described by me (*loc. cit.*), as also thallous compounds, to admit of a comparison of the methods. Commercial thallium in large quantities was submitted to a complete purification. We employed the electrolytic method, both alone and associated with M. Bautigny's process. The process followed for obtaining thallic oxide was as follows.

In our first experiments we obtained Tl_2O_3 by fusing thallous chromate with potassa. This process is not beyond criticism as regards the possible presence of chrome (though we have not detected it in our samples). I now employ simply the sulphate or nitrate, less commonly thallous chloride, melting them below a dark red heat with eight or ten times their weight of pure potassa. The hexagonal tablets of Tl_2O_3 formed are easily separated from the excess of potassium hydroxide or sulphate by washing with water until all alkalinity has disappeared and the potassium rays are no longer visible with the spectroscopy. The oxide thus prepared dries easily and does not lose oxygen below light redness. It is easily converted into thallous sulphate by means of sulphurous acid.

I have employed four different methods for the determination of the atomic weight :—

- Weight of thallium obtained by the electrolysis of thallous sulphate.
- Weight of thallium contained in Tl_2O_3 after conversion into Tl_2SO_4 and electrolysis.
- Weight of thallic oxide formed by the fusion of thallous salts with potassa.
- Proportion between thallium and oxygen on the reduction of Tl_2O_3 or hydrogen.

The first method gave for the atomic weight of thallium numbers varying from 203.52 to 203.69; the second yielded numbers comprised between 203.53 and 203.73; the third numbers from 203.44 and 203.79; and the fourth values comprised between 203.54 and 203.65.

The mean of these eleven determinations, selected from those which seem to have been most successfully executed, leads to the figure 203.62, a little below the value 203.7 which has of late been generally admitted without proof. Recent determinations of atomic weights generally tend to reduce the values adopted.—*Comptes Rendus*, cxvi., p. 580.

[M. Lepierre has thought it advisable to re determine the atomic weight of thallium. In so doing he remarks that "the value 203.7 has of late been generally admitted without proof." It may, in return, be fairly asked what guarantee does he furnish for the accuracy of his own results? If we compare his memoir with that of Mr. Crookes (*Philosophical Transactions of the Royal Society*, read June 20, 1872), we are at once struck with the fact that M. Lepierre omits, or at least makes no mention of,

those elaborate and minute precautions which Mr. Crookes found necessary in order to eliminate the possibility of error. M. Lepierre makes no mention of the balances employed, of any corrections for pressure and temperature, of any adjustment of weights, of precautions taken to ensure the purity of the chemicals employed, and especially of the thallium itself. He admits, indeed, the "possible presence of chrome" in one of his processes, though he was not able to detect it.

We cannot help noticing how completely, in a research of this kind, M. Lepierre omits all criticism of, or even mention of, the work of Mr. Crookes. It is a practice too common among our neighbours on the other side of the channel to ignore all work not published in the *Comptes Rendus* of the Academy of Sciences. It would have been more satisfactory, and we venture to say more truly scientific, had M. Lepierre criticised the work of Mr. Crookes, pointing out any additional precaution which might or could have been taken, and any error either in principle or in detail. In a matter of such fundamental importance as the determination of an atomic weight, this demand cannot be pronounced superfluous or excessive.

We, in turn, cannot well criticise M. Lepierre's results without a more thorough account of his procedures than he has seen fit to furnish.]

ON THE PURIFICATION OF WATER USED FOR STEAM-BOILERS.*

By R. JONES, Ph.D.

ALTHOUGH the injurious effects of boiler deposits is a common experience with all users of steam power, surprisingly little seems to be done in the way of combating the evil. From a paper by Betke, of Stettin, read at the last annual meeting of the (German) Society for Boiler Inspection, it appears that out of a total of 27,600 boilers inspected only 5480, or less than a fifth, were provided with any means at all of protection against incrustation, which is, I think, a sufficient proof that the importance of the subject has not as yet very deeply impressed those immediately concerned. And this, be it said, notwithstanding that the subject is one offering every possible inducement to its study.

A boiler, for example, fed with hard water, has to be laid off for cleaning oftener than one supplied with softened water, and the loss this entails, added to the cost of cleaning, may amount in the course of a year to almost the cost of a permanent plant for the purification of the water.

Then, again, boiler incrustation, on account of its bad conductivity, causes a greater consumption of coal. In a case referred to by Münter, the work of ten boilers was, after the erection of a suitable water softening plant, compassed by seven. Owing, also, to the bad conductivity of the incrustation, the boiler plates become over-heated, sometimes even red hot, and as a consequence are sooner destroyed. Many boiler explosions may, in fact, be traced to this cause, viz., to allowing the accumulation of too great a thickness of deposit. And then, lastly, there is the injury done to the boilers themselves by the operation of chipping off the deposit, which is by no means an inconsiderable item in the account.

* From the *Zeit. Angew. Chemie*, 1892, p. 15.—Communicated by H. H. B. Shepherd.

Any one of these reasons in favour of water purification, viz., less frequent laying off, saving in cost of cleaning, diminished consumption of coal, longer life of the boilers, and greater security against explosion, might indeed be held sufficient of itself to justify the erection of a water softening plant.

To what, then, can be attributed the prevailing neglect of this subject? Most frequently, I think, it arises from simple indifference, force of habit, and aversion to any kind of innovation; especially when expense is likely to be incurred, though some, no doubt, are deterred by the discouraging experience of their own or of others, due to experimenting with unsuitable plant. Then the number of doctors and empirics always ready to compete for the honour of ministering to the complaint makes the choice between them exceedingly difficult if one has not the opportunity of making the subject a special study, and, moreover, as every year sees new and presumably improved proposals brought forward, it is scarcely surprising that some should decide to wait until an absolutely perfect system shall have been produced.

Leaving, however, the conflict between the good and the better, let us pass on to consider what has already been accomplished, and I think we shall find that technical chemistry is even now able to satisfy the requirements of a good water purifying process.

In connection with water purification we have principally to consider three groups of salts.

1. Calcium and magnesium carbonates.
2. Calcium and magnesium sulphates.
3. Calcium, magnesium, and sodium chlorides.

The insoluble carbonates are held in solution by carbonic acid contained in the water. Simple boiling occasions the expulsion of the carbonic acid gas and the separation and precipitation of the carbonates as sludge, the sulphates and chlorides remaining in solution. In the boiler, however, in which naturally the same takes place as boiling in a beaker, the latter salts become more and more concentrated, since we are continually adding impure water containing these salts in solution and withdrawing pure water in the form of steam, so that in course of time the calcium sulphate which possesses a solubility of only 1 in 500 also begins to separate out. This separation, however, does not take place suddenly, and in the form of sludge, as in the case of the carbonates, but proceeds slowly, forming a crystalline incrustation enclosing the muddy carbonate deposit within itself. This coats the boilers, more especially on the parts in contact with the fire, and becoming baked on, produces the usual boiler incrustation. The magnesium salts and the chlorides remain in solution, the concentration never being carried so far as to cause the separation of these also. In addition, however, to the dissolved salts, many waters contain mechanical impurities such as earthy matter held in suspension, and these, through the constant ebullition, form into balls, which, settling down with the separated salts, become baked on, and so increase the quantity of the incrustation.

It is now apparent to the chemist by what means the purification of the water can be accomplished. The carbonates can be removed either by simple boiling or by withdrawal of the carbonic acid by addition of quicklime or caustic soda. The sulphates may be dealt with either by depriving them of their sulphuric acid by addition of barium chloride, or by precipitation of the lime and magnesia by sodium carbonate and caustic soda. The chlorides and alkaline salts must remain in solution, there being at present no practical means for effecting their removal. Their accumulation in too great quantity can only be guarded against by frequent sludging, and it is desirable for the sake of the boilers that this should be carefully attended to. But the chemical is the smallest, perhaps even the most unimportant, side of the question. The main problem is how the purification can be carried out.

In this connection valuable information is supplied by

the statistics of the Society for Boiler Inspection. In Betke's paper, already referred to, we find the following:

In 3800, or 15 per cent, softening of the water is effected inside the boilers themselves by decomposition of the calcium sulphate by sodium carbonate, barium chloride, or some other reagent; in 1400, or 5.5 per cent, the boilers are fed with chemically purified water; in 150 cases, or 0.6 per cent, the water is softened as above in the boilers, and the resulting precipitate caught by a dejector apparatus; and in 130 cases, or 0.5 per cent, the water is simply mechanically purified by filtration through sand or sponge. This last, however, lies outside the scope of our inquiry, as a simple filtration can be of use in only isolated cases, and then it is not merely useful but necessary; in all other cases an improvement of the water by such means is out of the question. As regards the 3800 boilers in which sodium carbonate or barium chloride is added direct, the society reports that this procedure mostly gives satisfaction. Where this process is suitable it is at any rate the cheapest, since no extra plant is required, and the only expense is the trifling cost of the reagents used. If it answers the purpose, it is of course necessary to maintain always a slight excess of soda in the boiler, as otherwise the incrustation, though diminished, will not be entirely prevented. Frequent sludging and regular testing of samples for excess of soda are also necessary to ensure a good result. Phenolphthalein answers well for this purpose, and a solution can be given to the workman in charge of the boilers.

In only the small number of 150 boilers, or 0.6 per cent, is the deposit removed by means of a dejector apparatus placed inside the boiler. Such an apparatus, however, is, as Fischer has shown, powerless to prevent the incrustation caused by the separation of calcium sulphate, and it is therefore necessary, in conjunction with it, to employ means to soften the water. The older apparatus of Popper and Schmitz appear to have been entirely abandoned. According to the statistics of the Boiler Inspection Society, the apparatus of Dervaux is used with 105 boilers, that of Schröder-Guben with 40, and that of Grimm, Natalis, and Co. with 5. The plan is favourably reviewed in the collective reports of the Society.

If, however, expense has to be incurred for fresh plant, it is certainly better to prevent the precipitate passing into the boiler at all than to provide means for its removal when there by a separate apparatus, and that this is the opinion of the majority is shown by the fact that against 150 boilers fitted with dejectors inside, there are 1400 fed with chemically purified water. Dervaux also, who alone has provided 75 per cent of these apparatus, must be of the same opinion, since two years ago he brought out a water purifying apparatus, which if not the best, is at any rate one of the best in existence.

Of the boilers fed with chemically purified water—

640	make use of the old plan of settling tanks.
280	" " Dehne's filter press system.
250	" " Gaiblet's apparatus (Humboldt's engineering works).
61	" " Bohlig and Heyne's plan.
54	" " the Dervaux plan.
255	" " the systems of Bérenger Stingl, Reichling, Hohenzollern, Klein, Schanzlin, and Becker, or Reinecke.

To attempt a detailed description of these various and in some respects very ingenious apparatus would go beyond the scope of this paper. In the settling-tank the water to be purified is carefully mixed with the proper chemicals and heat applied, and after the precipitate has settled out the clear water is drawn off. This process is both cheap and simple, and has the only fault of occupying too much space. As a rule one settling tank is not sufficient; indeed, for a large establishment a series

would be needed, and then the whole time of one man would be required to take charge of it.

The apparatus of Humboldt and of Dervaux are constructed on the principle of the settling tank. The water ascends from the bottom of the tank and impinges upon pillar-shaped plates placed one above the other, on which the sludge deposits. Reichling has a construction of his own with cloth and sand filters, Dehne and Klein, Schanzlin, and Becker filter direct through presses after boiling in small vessels with the chemicals.

The apparatus, *per se*, however, has nothing to do with the chemical purification of the water, and not one of these different systems can accomplish more than the simple settling tank, *i.e.*, produce clear water; they possess the advantages, however, of requiring but little space and of facilitating and simplifying the addition of the chemicals.

The following chemicals have been proposed for precipitating the salts which cause incrustation:—

1. Materials containing tannic acid. These are less effective than soda, and have the disadvantage of causing the water to froth; moreover, as they have not as a rule cheapness in their favour, they are very properly going more and more out of use.

2. Quicklime and barium chloride, first proposed by De Haën. To a given quantity of cold water milk of lime is added by degrees, whilst stirring, until it just commences to show a feeble reaction with turmeric or red litmus paper; solution of barium chloride, calculated according to the analysis of the water, is then added, the whole stirred and heated to boiling. The quicklime precipitates the carbonates of lime and magnesia in the form of a flocky precipitate, which carries down with it the otherwise slow-settling barium sulphate. In half an hour the water settles quite clear and can be drawn off. This process from the point of view of the removal of the salts causing incrustation is excellent. Beyond the chlorides originally contained in the water, nothing is now left but the lime of the gypsum (also in the form of chloride) and of course the excess of the reagents used. Herein, however, lies the weak point of the process. A small excess of barium chloride matters but little, but an excess of milk of lime produces an incrustation of the worst possible kind. This danger, however, it is said, can be avoided by the use of the lime saturator of Dervaux, in which milk of lime, which necessarily varies in strength, is replaced by saturated lime-water of constant composition. An excess of lime added in the form of lime-water cannot be otherwise than very trifling except through carelessness, and even then is easily removable by a little carbonate of soda. There is another point in connection with De Haën's system which should be mentioned, *viz.*, that the chlorides are liable to accumulate in the boiler water to an injurious extent. This evil, which is more or less common to every water purifying system, must be counteracted by daily sludging, and it is quite possible by this means in most cases to keep the concentration within harmless limits.

3. A third anti-incrustator which has been recommended is magnesia hydrate (Bohlig and Heyne's patent), of which the inspectors' reports speak very favourably (61 boilers are mentioned as being fed with water purified in this way); the result, however, can only be considered satisfactory if the water be poor in calcium sulphate.

4. The anti-incrustator in most general favour is carbonate of soda, either alone or in combination with quicklime or caustic soda. Even when used alone this reagent accomplishes all that could fairly be expected in the way of water purification. It is simple in application, precipitates the lime and magnesia almost completely, and has the distinct advantage which cannot be too highly esteemed, that the addition of too large an excess is perfectly harmless. When, however, carbonate of soda is used, it is very important that the boilers should be blown off regularly every day, or in time the concentration will reach a point when the solution will

have a higher boiling-point than that of water, and be liable to exert a corroding influence upon the plates, packing, &c., of the boilers.

(To be continued).

ON METALLIC OSMIUM.

By A. JOLY and M. VEZES

OSMIUM, as generally obtained by the method of Berzelius, *i.e.*, by igniting the sulphide in a crucible of carbon, is a powder or a spongy mass of a more or less deep blue colour, according to its state of division. It is then directly oxidisable in the air, and exhales a very strong odour of osmic acid. H. Sainte-Claire Deville and H. Debray obtained osmium in small crystals of a fine blue tinted with grey by passing fumes of osmic acid into a tube of carbon very strongly heated. The specific gravity of the metal has been successively represented by the numbers 7, 10, and 21.4; the specific gravity of crystallised osmium is 22.48.

H. Sainte-Claire Deville and H. Debray attempted unsuccessfully to fuse osmium by heating it before the oxyhydrogen blowpipe in a crucible of coke enclosed in a crucible of lime. If directly heated in the point of the blowpipe flame, the metal disappears rapidly, either by volatilisation or by conversion into the volatile peroxide. But even an experienced eye which follows the phenomenon attentively cannot detect in the morsels of osmium as they rapidly disappear the least trace of fusion. In order to solve this question osmium must be heated in a vacuum by means of a powerful arc. In consequence of its physical and chemical properties, which, however, vary according to the manner of its preparation, osmium approximates to the non-metals. According to Deville and Debray, it is the non-metal of the platinum family. Berzelius assimilates it to arsenic and Dumas to tellurium.

Perfectly pure osmium may be melted in the electric arc, and obtained in a metallic form comparable to ruthenium. On account of its oxidability, the poisonous character of its vapours, and to avoid losses by volatility, which render the experiments very costly (the lowest price of the metal being 1500 fr. per kilo.), it is necessary to adopt special arrangements. We operate in a closed apparatus traversed by a slow current of carbonic anhydride and in cupels of coke. If the metal is rapidly raised to the highest temperature of the arc, it melts without being appreciably volatilised.

We succeed badly if we operate in lime crucibles; in contact with the metal the lime is profoundly converted into a vitrifiable mass, with which the metal remains incrustated.

Melted osmium is very brilliant on the surface; the colour is still a bluish grey. Further experience must decide whether the metal is blue just as gold is yellow and copper is red. The fracture is crystalline, harder than iridium and ruthenium; it cuts glass deeply, scratches quartz, but is scratched by topaz; the best tempered files do not cut it. If thus melted osmium is not oxidised in the air at common temperatures.

Osmium as a metal may be compared to ruthenium; these two metals form a very distinct group—like rhodium and iridium on the one hand, and palladium and platinum on the other. The atomic volumes are almost identical.

	Atomic weight.	Specific gravity.	Atomic volume.
Ruthenium	101.4	12.06	8.40
Osmium	190.3	22.48	8.46

More refractory than all the other metals of the platinum group, they are more readily oxidised, and if heated to redness in oxygen they yield peroxides RuO_4 and OsO_4 .

They approximate greatly to Mn by their very extensive series of oxides of an acid character.

The double chloride $\text{OsCl}_4 \cdot 2\text{KCl}$ establishes the connection of the group with the platinum-palladium group, as well as with iridium. Ruthenium has no corresponding compound. Rhodium is similarly situated, and the compound $\text{PtCl}_4 \cdot 2\text{KCl}$ is not stable. The tetrachloride and its derivatives, so characteristic of platinum, are merely an exception for the three metals of the group, the atomic weights of which are comprised between 101 and 106. The double sesquichlorides $\text{Ru}_2\text{Cl}_6 \cdot 2\text{KCl}$ and $\text{Os}_2\text{Cl}_6 \cdot 2\text{KCl}$ connect them by rhodium and iridium.—*Comptes Rendus*, cxvi., No. 11.

SEPARATION OF MERCURY FROM THE METALS OF THE SO-CALLED ARSENIC AND COPPER GROUPS.

INAUGURAL DISSERTATION, GÖTTINGEN.

By K BÜLOW.

THE author treats the sulphides with a mixture of equal parts of equally concentrated solutions of potassium hydroxide and sulphide. In this mixture arsenic, antimony, tin, and mercury sulphides dissolve, whilst the sulphides of the copper group remain unaffected.

From the solution of the sulphides of mercury and of the arsenic group, the mercury is easily re-precipitated as sulphide on the addition of ammonium chloride. The author used a 15 per cent potassa-lye. It was mixed with a few drops of solution of potassium sulphide, and the clear solution was drawn off with a syphon from the subjacent black precipitate of iron sulphide.

In order to obtain the solution of potassium sulphide a 15 per cent potassa lye was divided into two parts; one of these was saturated with sulphuretted hydrogen, and the other part was then added. The clear solution was drawn off with a syphon from the precipitate which forms on prolonged standing in heat, and the solution of the potassium sulphide, like that of the potassium hydroxide, is preserved in well-fitting vessels. The solution of ammonium chloride used was purified from a possible proportion of iron by the addition of a few drops of ammonium sulphide, and the precipitate formed was filtered off.

For separating mercury from bismuth, 0.2 grm. mercuric chloride and an equal weight of bismuth oxide was dissolved in concentrated hydrochloric acid, and sulphuretted hydrogen was passed into the solution, which had been carefully diluted with hot water. After the bismuth has been precipitated it is largely diluted with hot water, and sulphuretted hydrogen is again introduced until the liquid is saturated.

After the precipitate has been filtered off and washed, the filter is perforated, and the precipitate is rinsed back into the beaker with hot water, to which a few c.c. of the above mixture of equal parts of potassa-lye and solution of potassium sulphide are added. The precipitate is then digested with from 20 to 25 c.c. of the above mixture; the liquid is then boiled once, diluted with hot water, and the bismuth sulphide remaining undissolved is filtered off. It is washed with water, to which a few drops of the mixture has been added. In order to bring absolutely all the mercury sulphide into solution, 10 c.c. of the mixture must be used to about 0.1 grm. of mercuric chloride taken.

The filtrate which contained the mercury was mixed with solution of ammonium chloride until no further separation of mercury sulphide takes place. The precipitate, which is at first finely pulverulent, readily clots together, and is deposited clear if the liquid is heated for some time on the water-bath.

The mercury sulphide is filtered, washed with water containing ammonium sulphide, and then returned to

the beaker together with the filter and covered with cold water. Potassium chlorate is then added, the whole well stirred up and mixed with a sufficiency of concentrated hydrochloric acid. The mercury sulphide dissolves rapidly and completely. The excess of chlorine is expelled on the water-bath, the filter residues are filtered out and washed with hot water containing hydrochloric acid.

The filtrate was largely diluted, heated to about 90° , and saturated with sulphuretted hydrogen. If it is not sufficiently diluted, and if the solution is not heated, the precipitate settles very badly, and the quantity of mercury is found deficient up to 15 per cent. The mercury sulphide was filtered through a filter, dried at 102° and weighed, washed with sulphuretted hydrogen water to which a few drops of concentrated hydrochloric acid have been added, dried at 102° , and weighed.

The determination of the bismuth can be effected according to one of the ordinary methods. This process effects a complete separation of mercury from bismuth. Mercury may be separated from copper, silver, and lead in a quite similar manner.

The method is, however, not applicable to the separation of mercury from cadmium, since a large part of the mercury sulphide remains undissolved along with the cadmium sulphide. Nor can the separation of the two metals be effected by treating the sulphides with nitric acid, since a considerable part of the mercury sulphide remains undissolved along with the cadmium sulphide. The author shows that zinc sulphide cannot be separated from mercury sulphide by digestion with the above mentioned mixture.

For separating mercury from arsenic, 0.2 grm. each of arsenious acid and mercuric chloride were dissolved in concentrated nitric acid, and the excess of the latter was evaporated off as far as possible. After the solution obtained had been largely diluted, it was saturated with sulphuretted hydrogen. The precipitate formed was filtered off after standing for a long time, and digested as above described with the solution already named. The clear solution thus obtained was slightly diluted, boiled up, and mixed with solution of ammonium chloride until no further separation of mercury sulphide occurs. It is then heated on the water-bath and the mercury sulphide is filtered off. The arsenic sulphide in the filtrate is determined by a usual process, whilst the mercury is determined as above described.

In separating mercury from antimony, 0.2 grm. antimony oxide and an equal weight of mercury chloride were dissolved in concentrated hydrochloric acid. It was then oxidised with potassium chlorate, mixed with tartaric acid after the expulsion of the excess of chlorine, diluted, heated, and the solution saturated with sulphuretted hydrogen. The further treatment may be inferred from what has been said on the separation of mercury and arsenic.

Whilst this method gives good results for the separation of mercury from arsenic and antimony, it is not applicable to the separation of mercury from tin. Ammonium chloride throws down from the solution of the sulphides a part of the tin, along with the mercury sulphide, and some mercury remains in solution along with the main quantity of the tin.

Of course, mercury can be separated by the above method if several of the above metals are present simultaneously, cadmium and tin being excepted.—*Zeit. Anal. Chemie*, vol. xxxi., p. 697.

Examination and Correction of the Saccharometer Scale.—K. Ulsch (*Zeit. für Brauwesen*) suspends the instrument from the hydrostatic balance, and for the several degrees of the scale determines the loss of weight which the instrument undergoes when plunged into pure water at 14°R . To find the true value of this degree of the scale, the weight of the saccharometer is divided by the loss of weight.

THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

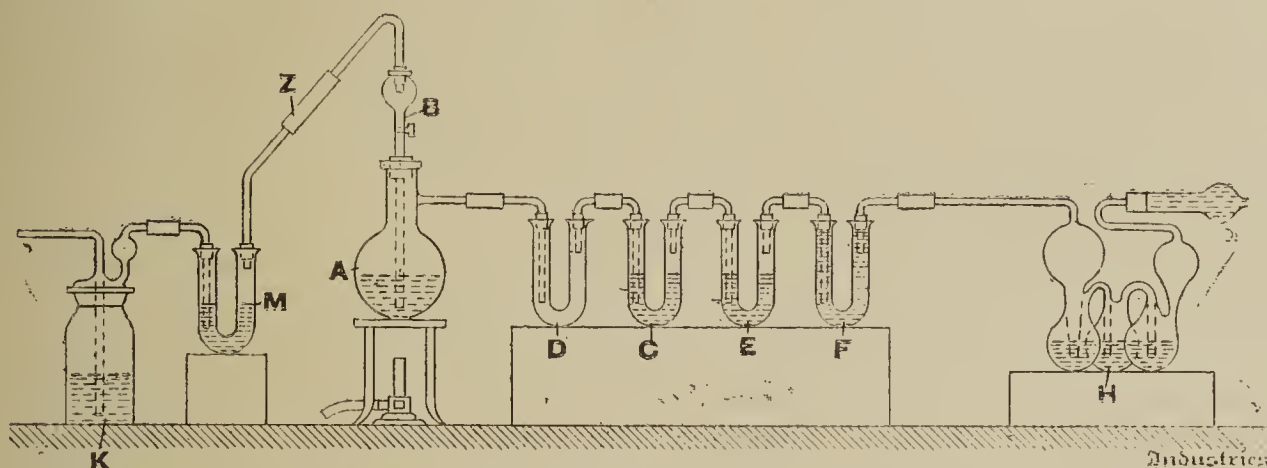
(Continued from p. 162.)

Total Carbon.—There are at least two conditions in which carbon may exist in iron and steel, viz., (1) in chemical combination with the iron, and (2) in the free state as graphite or graphitic carbon. In steel it is considered that there is a third form of carbon termed "cement carbon," which has considerable influence upon the quality of the metal under varying conditions of temperature, &c. As is well known, upon dissolving iron or steel in hydrochloric acid, the iron enters into solution as ferrous chloride with the evolution of hydrogen, which, being in the nascent condition, combines with any combined carbon present, forming volatile hydrocarbons, while the graphitic carbon remains intact. If, however, the iron be dissolved in such a manner as to prevent the evolution of hydrogen, no hydrocarbons are formed, and the combined, together with the graphitic carbon, is deposited in an insoluble form, which may be collected and burnt, and the resulting carbonic acid (CO_2) weighed directly or indirectly. Such is the action when the metal is treated with a solution of ammonium cupric chloride or

air, and wash with water as long as any of the fibre runs through. The next step is to extract the copper from the carbonaceous residue. This is accomplished by adding hydrochloric acid together with a fresh portion of the chloride solution, and digesting until the whole of the metal has dissolved. When this is effected pass the supernatant solution through the asbestos filter, throw on the residue by means of a fine jet of water, wash several times with hot hydrochloric acid, and finally with water, until a drop of the washings after acidification with nitric acid gives no opalescence with silver nitrate. The residue is now ready for combustion.

Determination of the Total Carbon in the Crude Residue.—Either a dry or wet method of combustion may be employed for the determination of the carbon in the crude residue. Amongst the latter is Ullgren's, the principle of which is that, upon treating the carbonaceous residue with chromic and sulphuric acids, the carbon is oxidised into carbonic acid (CO_2), which is weighed either directly or indirectly.

The apparatus employed is shown in Fig. 1, below. As will be seen, it consists of a small flask, A, of about $\frac{1}{4}$ litre capacity, connected with a system of tubes D C E F, H containing reagents for purifying, drying, and absorbing the carbonic acid evolved. The neck of the flask is fitted with a caoutchouc cork, through which passes the stop-



copper sulphate; the iron displaces the copper and enters into solution, while the combined and graphitic carbon, together with copper, are deposited.

The determination of the total amount of carbon consists of two operations—(1) the preparation of the carbonaceous residue for subsequent treatment, and (2) the determination of the carbon contained in this crude residue.

Preparation of the Carbonaceous Residue.—Dissolve 280 grms. of ammonium cupric chloride† crystals in a litre of water, and into 120 c.c. of this solution, contained in a beaker, add 5 grms. of the iron or steel, and digest at a gentle heat‡ with constant stirring until complete disintegration is effected. Should the liquid become colourless, or nearly so, more of the chloride solution should be added, and on no account must it be allowed to approach boiling temperature, as this causes the silicon to acquire a condition which retards the operation of filtering. Upon complete disintegration, allow the residue, composed of combined and graphitic carbon and metallic copper, to subside, and decant off as much as possible the supernatant liquid; passing it through an asbestos filter constructed as follows:—A piece of glass tubing, $\frac{1}{2}$ in. diameter and 6 in. long, is contracted at about 1 in. from one end, and this narrow portion loosely plugged with glass wool. On the top of this a layer of finely divided asbestos fibre is placed, previously ignited in a current of moist

cock funnel B, reaching to nearly the bottom, and also a tube bent at right angles, connected with the tubes K M. The asbestos filter containing the crude carbonaceous residue, obtained as above, is transferred to the flask A by inverting the filter tube in the neck and gently blowing it out, rinsing in with the smallest quantity of water possible the portions adhering to the sides. Now add to the flask about 50 c.c. of concentrated sulphuric acid, allow to cool, insert the caoutchouc cork, and connect with the system of tubes. Add 8 grms. of chromic acid crystals dissolved in a little water through the funnel B, close the stop cock, and heat the flask gently, so regulating it as to maintain an even and constant evolution of gas. The residue is immediately attacked by the acids, carbonic acid being formed. The gas as it is evolved passes over in the tube D, containing a solution of sulphate of silver in sulphuric acid, which retains any chlorine, and from thence it bubbles through the tubes C E, containing respectively sulphuric acid and calcium chloride, where the water (moisture) is absorbed. It next enters the *previously weighed* bulb tubes F, containing a solution of caustic potash (1 part alkali in 1½ water), which almost completely absorbs the carbonic acid, but a small portion, together with some of the water of the potash solution, is carried over by the unabsorbed gas. To collect this, which would otherwise be lost, and thus occasion serious error, a weighed U-tube, H, is attached, containing in the limb nearest the potash bulb granulated soda-lime, while the other is filled with calcium chloride.

As soon as heavy white fumes appear in the body of the flask, connect the tube H with an aspirator, open the

* From *Industries*, February 24, 1893.

† Copper sulphate may be advantageously used; we deem it preferable.

‡ Fresenius recommends that solution be effected at ordinary temperature, as, upon warming, a small quantity of gas containing carburetted hydrogen is evolved.

pinch-cock, z, attached to the caoutchouc tubing at the end of the glass tube protruding through the cork in the mouth of k, which is kept closed during the first part of the operation, remove the source of heat, and draw a current of air—which will be freed from moisture and carbonic acid in passing through k m, containing respectively caustic potash and calcium chloride—through the apparatus until it is thoroughly cool, when the bulb tube r is re-weighed; any increase in weight is due to carbonic acid (CO_2). The tube n is likewise re-weighed at the conclusion of the experiment, and the increase of weight, if any, deducted from the first weight of r. Carbonic acid contains 27.27 per cent of carbon. It is obvious that the apparatus must be perfectly air-tight, and also that the chemicals employed be free from organic matter. To guard against the possibility of error through this latter source, it is advisable to perform a blank experiment with the reagents only.

Calorimetric Determination of Combined Carbon.—As previously stated, iron and steel may contain carbon in at least two conditions, either in the free state, or graphite carbon, as it is termed, or in chemical combination with the iron. The method just described furnishes the amount of total carbon present and leaves us altogether ignorant of the proportion present in the several conditions. And as from the amount of combined and graphitic carbon, together with other constituents, although in a less degree, contained in iron or steel, we are able to determine the suitability or otherwise of the metal for certain purposes, as also to classify it, it becomes necessary to determine the quantities present respectively in the two conditions.

The combined carbon in steel may be determined by combustion, but in the laboratories connected with iron and steel works, where a large number of estimations have to be performed during the course of the day, the method is rarely brought into requisition, as it involves both considerable time and labour. The method commonly employed is Eggertz's calorimetric test, the principle of which is that upon dissolving iron or steel containing combined carbon in nitric acid free from chlorine, a brown coloured solution is produced, varying in intensity or depths of tints in proportion to the amount contained in the metal. It is therefore a simple matter to determine by this method the combined carbon contained in any nitric acid solution of the metal by comparing with that obtained upon treating a "standard" containing a known amount of combined carbon in a precisely similar manner. Under certain conditions, and in the hands of a skilful and intelligent operator, Eggertz's test gives fairly good results, but with some classes of iron and steel it entirely fails. This is the case with specimens that have been hardened or contain over 1 per cent of carbon. It is obvious that for the carrying out of the method, standard steels, in which the combined carbon has been carefully determined by combustion, are required, and it is requisite that these should be of the same make and contain as near as possible a like amount of combined carbon as the samples under examination. Artificial coloured standards are, in our opinion, of no use whatever; and it is impossible to get accurate results by comparing a standard high in carbon with a low carbon steel.* The *modus operandi* of the calorimetric method is as follows:—Weigh out into a dry test-tube, $\frac{1}{2}$ in. diameter and about 6 in. long, 0.20 grm. of the same quantity of a standard steel. To each add 5 c.c. of nitric acid, specific gravity 1.20, free from chlorine, and when all action is at an end, place the tubes in a vessel containing water kept at boiling temperature for fifteen minutes. At the end of this period the tubes are simultaneously withdrawn, any crust adhering to the inside of them being removed by causing the solution to flow over it, and placed in a vessel containing cold water.

When perfectly cold the solution of the standard steel

is transferred, without loss, to a graduated tube closed at one end of 200 c.c. divided into 1.10th c.c. capacity, the test-tube rinsed out with a little cold water, the washings added to the bulk of the solution, which is now diluted, until the volume occupied is a power of the percentage of combined carbon which it contained, and mixed by closing the open end of the tube with the thumb, and inverting two or three times. Supposing the standard to contain 0.35 per cent combined carbon, the solution would be diluted until the volume occupied measured 7 c.c., which is the 0.05th power of 0.35. The solution of the specimen under examination is next transferred to a tube of a like calibre and graduation as the standard; the last portion rinsed in with the least possible quantity of cold water, and the solution thoroughly mixed *without dilution*. If it be found upon comparing the colour of the two liquids, by holding the tubes side by side before a window with a piece of unglazed paper behind them, that the colour of the standard is lighter than the sample being analysed, the latter is cautiously diluted with small quantities of cold water, mixing and comparing after each fresh addition until the tints are of equal intensity. The volume in c.c. occupied by the solution of the sample—when this is obtained—multiplied by the power, of which the volume occupied by the standard is of the carbon it contains, will yield the percentage of combined carbon. If, however, upon comparing the two solutions the standard is found to be darker than the sample, the volume of the former is doubled, and only half the volume of the latter taken upon the attainment of equal tints. If the operator, upon the obtaining of equality of tints, will reverse the position of the tubes, placing the one formerly held to the right to the left, he will find in all probability that the one now held to the right will seem slightly the darker of the two. He should therefore make it a rule to hold the standard solution always to the same side, either to the right or left.

With specimens containing minute portions of combined carbon, the resulting solutions are invariably of a greenish colour. This to a certain extent may be obviated by employing half the volume of nitric acid, both for the samples and standard steel.

As the nitric acid solution of the metal obtained in the calorimetric method becomes decomposed after a short exposure to the light and atmosphere, it is not possible to make the standard solution serve for a whole day's work, a fresh standard must be prepared with each batch of determinations. Even were this admissible, the fact that, to obtain anything like accurate results, the conditions, as regards temperature, &c., under which the solution is effected must be *precisely* similar, would render it impracticable. This entails both time and labour, which some chemists obviate by employing permanent standards composed of burnt sugar, metallic salts, burnt coffee, &c. We strongly condemn this practice on account of the very necessary condition above stated being totally ignored. Stead has devised a method for the calorimetric determination of combined carbon, in which 1 grm. of the metal is dissolved in 12 c.c. of nitric acid 1.20 specific gravity, diluted with 30 c.c. of water, 13 c.c. of a caustic soda solution 1.27 specific gravity added, which results in the depth of tint being considerably intensified, filtered through a dry filter, and compared, in a special form of chromometer, with the colour of a standard steel treated in a precisely similar manner. A chromometer for the calorimetric determination of carbon has also been devised by Mr. C. H. Ridsdale, full particulars of which appeared in the *Journ. Soc. Chem. Ind.*, vol. vii., p. 70–73.

The colour test for carbon is only applicable to steel when produced under like conditions. Hammered steel frequently shows more combined (colour test) carbon than is originally contained in the ingot after hardening or drawing out the ingots.

In the latter there is always a portion of carbon which cannot be termed graphite, but existing in a state insensible to the colour test, and this portion is found to

* The other constituents should also be nearly as possible present in the same proportions.

increase according to the total amount of carbon in the metal, as also the rapidity with which it is cooled. Therefore in some degree the composition of steel seems modified, like common grey iron in which the proportion of graphite is more or less in accordance with the rate of cooling. Discrepancies in the determination of combined carbon by the colour test of the same cast of steel have thus been explained.

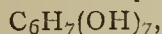
(To be continued).

THE USE OF THE TERM "CARBOHYDRATES."

By W. E. STONE, Ph.D., Purdue University, Lafayette, Ind.

It has frequently happened in the history of chemistry that names and terms have lost their original significance so soon as the knowledge of the bodies to which they were applied has become more extended. "Organic" chemistry is better named the "chemistry of carbon compounds"; the "aromatic" bodies have disappeared in the broader designation of benzene derivatives. In the same way it appears that we have reached, or already passed, a transition stage in the use of the term "carbohydrates." Treatises on chemistry still retain the old definition of the term, while those familiar with recent progress in this field no longer feel themselves restricted to these ancient limits. It is the purpose of this paper to consider the present status of this subject.

Von Lippmann, in his work "Die Zuckerarten und ihre Derivate," adopts Fittig's view that the carbohydrates are derived from the hypothetical heptatomic alcohol—



which, by loss of water, forms the simple or complex anhydrides, $\text{C}_6\text{H}_{12}\text{O}_6$ or $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, known as sugars. His treatment ignores the existence of any carbohydrate with less than six carbon atoms, although he says that, with the (at that time, 1882) slight knowledge of the constitution of the carbohydrates, it was impossible to regard this definition as final and complete.

In 1888 appeared Tollens's "Handbuch der Kohlenhydrate," in which the definition of "carbohydrates" was limited strictly to the bodies composed of C, H, and O, containing six carbon atoms, or some multiple of six, and H and O in the same proportion in which they are found in water. But already Kiliani had shown that arabinose, which had long been regarded as a true carbohydrate on account of all its reactions, had really the composition $\text{C}_5\text{H}_{10}\text{O}_5$. Moreover, it had already been established that the best-known sugars, such as dextrose, levulose, galactose, and arabinose, had the constitution of aldehyds or ketones of the hexatomic, respectively pentatomic, alcohols. In anticipation, therefore, of evident progress along this line, Tollens remarks, in his Preface, that such bodies as arabinose and the impending erythrose might well be regarded as carbohydrates, but he retains the hexatomic nature as a requirement for the "true carbohydrate," and puts all non-conforming but similar bodies under the head of "den Kohlenhydraten nahestehenden Körper."

Up to this time a sort of understanding had prevailed that the carbohydrates were exclusively products of natural forces. It had also been noted that these bodies gave certain reactions, which were also presented as a basis for the classification given.

These reactions, as stated by Tollens, are—

1. Reduction of alkaline metallic solutions.
2. Rotation of polarised light.
3. Subject to alcoholic fermentation by yeast.
4. Formation of levulinic acid.
5. Formation of characteristic compounds with phenylhydrazin.
6. Certain colour reactions.
7. Solubility, either before or after hydrolysis.
8. Decomposition by heat.

All of which hold strictly true for the hexatomic carbohydrates. This classification was probably as liberal as the state of knowledge at that time would justify.

But this classification is evidently arbitrary, and ought not to have weight in comparison with any classification based on chemical constitution. If a similar constitution can be proven for a series of bodies, the fact that they respond to certain reactions will only be additional proof of their relationship. Such reactions must, of course, be general in their nature, while special reactions will only serve to characterise individuals. In this way the class of carbohydrates must eventually include only bodies of certain constitution, while the characteristic reactions will be limited to a smaller number, of more general application. A similar development has taken place in the manner of classifying the hydrocarbons, alcohols, acids, glycerides, &c.

Of the carbohydrates conforming to the old definition, dextrose, levulose, galactose, and mannose are types. They respond to the reactions given, and have been found to possess the constitution of ketones or aldehyds of the hexavalent alcohol, $\text{C}_6\text{H}_{14}\text{O}_6$. But we know two bodies of the formula $\text{C}_5\text{H}_{10}\text{O}_5$, arabinose and xylose, which are also aldehyd alcohols, and which give the same reactions as their homologues, with the exception of fermentation and the formation of levulinic acid. Again, we know an aldehyd of the tetratomic alcohol erythrit, called erythrose, of the formula $\text{C}_4\text{H}_8\text{O}_4$, which responds to the same general reactions as its homologues. Glycerose, $\text{C}_3\text{H}_6\text{O}_3$, has also been studied, and found to correspond to the others of the series in constitution and general reactions. It is even fermentable with yeast, like the regular carbohydrates, which shows this to be an intermittent reaction when applied to an homologous series. Beginning again with the group $\text{C}_6\text{H}_{12}\text{O}_6$, we find that there have been prepared synthetically three other homologues representing aldehyds, respectively of the hept-, oct-, and nonatomic alcohols. These also respond to the general reactions given, except that they do not form levulinic acid. Heptose and octose do not ferment, but nonose, with its multiple of three carbon atoms, is fermentable.

It is no argument against the carbohydrate nature of these bodies to say that they do not occur in nature, since two of the hexoses (galactose and mannose) have never been found free, but are only known as derivatives of certain natural products. In this respect they are on precisely the same footing as arabinose, xylose, erythrose, and glycerose.

It appears, therefore, that we have an homologous series of aldehyd or ketone alcohols of the general formula $\text{C}_n\text{H}_{2n}\text{O}_n$ with these common properties:—1, sweet to the taste; 2, optically active; 3, reducing alkaline metallic solutions; 4, yielding with phenylhydrazin characteristic crystalline compounds. Other reactions, such as great solubility, decomposition by heat, and colour reactions, are less characteristic, although possessed in common. Those containing three, or multiples of three, carbon atoms undergo alcoholic fermentation with yeast, and this periodical reaction seems an additional argument for their common nature. Individually they yield, when heated with strong acids, characteristic derivatives; for instance, the pentoses yield furfural, the hexoses levulinic acid; others have not been carefully studied in this direction.

Following are the members of this homologous series which are known, although several additional isomers are possible:—

Triose, $\text{C}_3\text{H}_6\text{O}_3$.—Glycerose.

Tetrose, $\text{C}_4\text{H}_8\text{O}_4$.—Erythrose.

Pentose, $\text{C}_5\text{H}_{10}\text{O}_5$.—Arabinose, xylose.

Hexose, $\text{C}_6\text{H}_{12}\text{O}_6$.—Dextrose, levulose, galactose, mannose, all in isomeric forms.

Heptose, $\text{C}_7\text{H}_{14}\text{O}_7$.—Heptose.

Octose, $\text{C}_8\text{H}_{16}\text{O}_8$.—Octose.

Nonose, $\text{C}_9\text{H}_{18}\text{O}_9$.—Nonose.

By the definition of carbohydrates, now extant, only the hexoses are included. It is the purpose of this paper to propose the extension of this term to all members of the homologous series, on the basis of a common constitution, *viz.*, as aldehyds or ketones of the normal polyatomic alcohols of the aliphatic series. As characteristic properties of all these, must follow their behaviour toward polarised light, toward alkaline metallic solutions, and toward phenylhydrazin.

Such a classification would exclude the bodies of the cellulose group, of which there are many, more or less well defined. But it is not yet evident that they possess a constitutional relation to the bodies under discussion, and have certainly no claim to be classed with the aldehyd or ketone alcohols because convertible into them.

As for the disaccharides of the hexoses, to which belong sucrose, lactose, &c., if it be true, as supposed, that they are anhydrides or ether-like forms of the hexoses, then they are entitled to a place among carbohydrates as derivatives or modifications of the same.

E. Fischer proposes to apply the name "sugars" to all the members of this homologous series, to which he has lately added the glycol-aldehyd $C_2H_4O_2$ as the simplest possible example. The popular conception of the properties of a sugar are not, however, easily reconciled with the properties of some of these bodies, while "carbohydrates" at least possess some reference to their empirical composition. With regard to glycol-aldehyd, moreover, its optical inactivity would exclude it from the list under the conditions here proposed, although its constitution undoubtedly satisfies the requirements.—*Science*.

THE PERIODIC ARRANGEMENT OF THE ELEMENTS.

By P. J. F. RANG.

THE general plan of the Table is to arrange the elements in their respective series, so that all the allied elements should come in the same vertical row. The Table has been divided into four groups, A, B, C, and D, whereof the end group A contains the strongest positive elements, and the other end group D the strongest negative elements. In the centre group B are the elements with high melting points; they are all remarkable for their molecular combinations. At one side of this group are the anhydro combinations; at the other side are the amin, carbonyl, and cyanogen combinations; in the other centre group, C, are the heavy metals that have low melting points. If groups A and D be split up vertically in respectively three and two parts, the Table presents seven vertical groups, and horizontally seven more or less complete series. Each group in each of the series 2 and 3 are represented with one element. The octave appears also both horizontally and vertically in the Table; this is in conformity with a great scientific authority, who tells

us that the octave is extended over all nature, and that it is to be found in two diametrically different directions. The atomic weight of Li—the first periodic alkali element—seems also to show the octave.

Wimmerby, Sweden.

TECHNICAL ESTIMATION OF LEAD.

By ALBERT H. LOW.

PROVIDE three wash-bottles containing the following solutions respectively:—

Distilled water, or, at least, chlorine-free water.

Dilute sulphuric acid. One part C. P. acid to 9 parts chlorine-free water.

Chloride of ammonium. Make a saturated solution of the commercial chloride in common water: transfer this to the wash-bottle as required, and heat to boiling for use.

Treat 1 grm. of the ore in a covered Griffin beaker, of about 150 c.c. capacity, with 10 c.c. of a mixture of equal parts strong pure nitric acid and water. Heat carefully until the ore is pretty well decomposed, and then add 10 c.c. of pure strong sulphuric acid, and heat strongly until all the nitric acid is expelled and the sulphuric acid is boiling freely. This is best done over a small naked flame, taking care that the flame does not touch the beaker above the liquid. A 250 c.c. flask has some advantages over a beaker for this decomposition, but is harder to wash out subsequently. Cool and add 10 c.c. of the above dilute sulphuric acid. Then add 2 grms. of Rochelle salt, roughly weighed, or even guessed at. When this is dissolved add 40 c.c. of distilled water, and heat to boiling. Allow to stand and settle two minutes, and then filter and wash with the dilute sulphuric acid. Now spread the filter out carefully on a watch-glass, and wash the contents back into the beaker with a stream of the boiling hot chloride of ammonium solution. Heat the beaker again until all the sulphate of lead has dissolved, adding more chloride of ammonium if necessary. Again filter, receiving the filtrate in a clean flask, and wash the filter thoroughly with the hot chloride solution. Small amounts of sulphate of lead may be easily dissolved upon the original filter, without removing from the funnel, by simply washing with the hot chloride solution. Place in the filtrate three pieces of sheet aluminum, each about one-sixteenth of an inch thick by five-eighths of an inch wide and an inch and three-quarters long. The aluminum should be the purest obtainable, as the commercial article leaves an appreciable residue of silicon on dissolving. Heat the contents of the flask to boiling. If the bulk of the filtrate has been kept down to 75 or 100 c.c., the lead will be completely precipitated with five minutes' boiling. Remove from the heat, and shake the mixture around to collect the lead. The aluminum should appear clean, with but little lead adhering to it. Fill the flask with

Valence.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	I.	II.	III.	IV.	V.	VI.	VII.
Series.															
1.	Li	Be	B	C	II
2.	Na	Mg	Al	Si	N	O	F
3.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	P	S
4.	Rb	Sr	Y	Zr	Nb	Mo	..	Ru	Rh	Pd	Ag	Cd	Tn	As	Cl
5.	Cs	Ba	Di	..	Ta	W	..	Os	Tr	Pt	Au	Hg	Sn	Sb	Br
6.	..	Ms	..	Th	..	U	Pb	Bi	I
7.															
Group 1.	2.	3.					4.					5.		6.	7.
	A.						B.					C.			D.

Di here represents all the triads that are between Ba and Ta. H may not be exactly in its true place, still it cannot be very far from it.

cold water, and transfer the entire contents to a large casserole. Wash the lead twice by decantation, and, after filling up the casserole the third time, remove the aluminum with the hand, rubbing off any adhering lead under water. Again decant and then rinse the lead into a small porcelain dish. Pour off the water and, with an agate pestle, collect the lead as nearly as practicable into one piece, and press it into a thin hard sheet. Wash this once or twice with distilled water and then with alcohol. Dry the lead carefully, which should not cause any oxidation whatever, and then brush it into the scale-pan and weigh. The lead is practically free from silver, gold, copper, antimony, bismuth, arsenic, &c. A deduction of 3 per cent is a fair allowance for arriving at the fire assay of a pure ore of the same grade. As but little of the aluminum is dissolved, the same pieces may be used repeatedly.—*Journal of Analytical and Applied Chemistry*, vi., No. 12.

NOTICES OF BOOKS.

Diseases Incident to Workpeople in Chemical and other Industries. An Address Delivered before the Chemical and Physical Society of University College, London. By WATSON SMITH. London: Eyre and Spottiswoode, 1893. 8vo., 34 pp.

THIS judicious and timely pamphlet is substantially a review of Dr. J. T. Arlidge's work, "The Hygiene, Diseases, and Mortality of Occupations," and it has been called forth by certain ill-judged and sensational notices of the same book which have been contributed to daily papers by certain unqualified writers.

We do not, of course, even if we had the power, object to the discussion of technical and sanitary questions in the daily papers. On the contrary, we consider it a good feature, since hygienic evils and their remedies will thus be brought under the notice of thousands of persons to whom the scientific, medical, and technical journals are sealed books.

But we think the public has every right to demand that such subjects should be handled only by experts, physicians, pathologists, chemists, and technologists; that all exaggeration and everything of a sensational character should be avoided, and that all attempts to make the questions subserve the purposes of faction should be rigorously excluded.

Now these essential features are conspicuous by their absence in the series of notices which have appeared in a certain morning paper. As Mr. Watson Smith puts it, "Dr. Arlidge's eminently correct and sober title is changed for the highly sensational and exaggerated one 'Death in the Workshop.'"

In the same morning paper we read: "For the most part Dr. Arlidge's moral is to exhibit the avoidable shortening of the lives of our brothers and sisters for the simple reason that *it suits* (!) certain manufacturers to produce their wares under conditions which make healthy living impossible, and that it has not yet occurred to the State to step in and prevent them." What would the newspaper writer just quoted think if told that it *suits* certain journalists to delude the British workman into the belief that he is ill-treated for the convenience of the manufacturer? If such journalists were really acquainted with the facts of the case they would know that the workman obstinately resists every improvement which might prolong his life. They hold, as Mr. Watson Smith tells us, and as we know from abundant personal observation, that "the best and only cure for any result of inhalation of chlorine gas, or dust, or acid vapour is a good wash down with rum or whiskey. The custom has thus sprung up of going to the office on such occasions when frequently money is allowed and the alcoholic is taken." This

practice is, to our knowledge, no better than a superstition. If an oxide of nitrogen has been inhaled we have repeatedly found, in ourselves and others, that relief is most quickly and completely obtained by taking small sips of acetic acid as strong as it can be endured.

Without, however, venturing into the perilous region of the temperance question, we cannot refrain from quoting the authoritative utterance of Mr. A. E. Fletcher, H.M. Chief Inspector under the Alkali Acts, that "there is nothing deadly about an alkali works except the dirt and the drink."

Dr. C. O. Weber, a friend of Mr. Watson Smith, here quoted, declares that "habitual drinkers are absolutely unable to work in an atmosphere containing a quantity of aniline, which upon men of temperate habits has no effect whatever. The same is the case with the vapours of nitrobenzene." This fact may put in a stronger light the dangers of the fraudulent addition of nitrobenzene to factitious wines in order to impart to them the Burgundy flavour!

Mr. Watson Smith tells his hearers that the British chemical manufacturers, so far from seeking to obstruct sanitary improvements in their works and their processes, have in their organ, the *Journal of the Society of Chemical Industry*, a sanitary department, and "welcome all the light they can gain."

It scarcely falls within our sphere, but we may still mention that the hours of labour in the least agreeable departments of the alkali trade are short. At the establishments under the "Alkali Union" the week's work for bleaching-powder packers is thirty-four hours, and the average rate of wages 5s. 4d.

At the Widnes Alkali Works the average weekly earning for the same work is from 50s. to 60s. per week of thirty-six hours.

Some idea of the fairness of the recent newspaper criticisms of Dr. Arlidge's work may be judged from a comparison of the following statements:—Says the first of the articles on "Death in the Workshop," "Dr. Arlidge has investigated such entirely deadly facts as that the average life of the blacksmith is eighteen years." But if Dr. Arlidge is allowed to speak for himself he declares that "the occupation of a blacksmith must, on the whole, be pronounced a *healthy* one." He adds that "in commenting upon the disorders of blacksmiths the prevailing intemperate habits of these workmen must be noted."

We hope to return to a subject of so vital importance both for public health and for our national industries.

Soap Manufacture. A Practical Treatise on the Fabrication of Hard and Soft Soaps; and Analytical Methods for the Determination of their Chemical Composition, together with a short account of the Materials Employed. By W. LAWRENCE GADD, F.C.S. London: G. Bell and Sons.

THIS work forms a member of the series known as Technological Handbooks, and is calculated to be very useful at the present day.

No one can venture to assert that any new source of fatty matters or of alkalis suitable for soap making has been discovered. No new light has been thrown on the process of saponification. Yet, for all this, the trade has undergone a curious revolution. New soaps, substitutes for soaps, and adjuncts to soaps appear in all directions. The columns of the Press and the interiors of public conveyances display advertisements of these detergents, always sensational and often illustrated. Mr. Gadd would have merited well of the straightforward soap manufacturer and of the general public had he added to his work a few analyses of some of the more notorious of these recent claimants for patronage.

The first, or introductory, chapter of this work consists of a general account of the scientific principles of soap making.

In the second and third chapters we find an account of the materials as actually used. It is not encouraging to find bone-fat, kitchen-fat, and fuller's-fat ranking among the "more important" fatty substances worked up by the soap maker.

The dirty character of palm oil—the rubbish sometimes reaching 30 per cent—is duly noticed. The properties which water should and should not possess, and its purification, are next expounded. The Leblanc process for the manufacture of soda is described at a length scarcely requisite at present. We must regret that there is scope for the remark that Baumé's hydrometer is in use in some soap works. It has not a single advantage in comparison with Twaddell's instrument, and some very palpable demerits.

The analysis of soap is considered in a separate chapter, and there are, besides, instructions for the examination of the materials. The prevalent impurities in soaps, such as china-clay, magnesium silicates, &c., are touched upon, perhaps too leniently.

Upon the whole, this work may be characterised as decidedly useful and opportune. Common as soap is, a knowledge of its legitimate composition and properties is by no means common.

Pharmaceutical Society of Great Britain. Chemical Papers from the Research Laboratory. Edited by WYNDHAM R. DUNSTAN, M.A., Professor of Chemistry to the Pharmaceutical Society, and Director of the Research Laboratory. Vol. I., 1892.

It is pleasant to see a professional organisation taking into consideration something worthier than instituting and multiplying examinations. The Pharmaceutical Society has formally organised a "Research Laboratory," which has now been in operation for three years, and has done no small quantity of work. The papers here inserted, which have already appeared in the *Transactions* respectively of the Royal, the Chemical, the Pharmaceutical, and the Physical Societies, are of course of special moment to pharmacists. Some, however, are more widely interesting. Among these must be placed a memoir by Prof. W. R. Dunstan on the occurrence of skatol in the vegetable kingdom. This is of general scientific value, as breaking down another of the imaginary distinctions raised between plants and animals.

The method for the purification of mercury by distillation in a vacuum, by Messrs. Dunstan and Dymond, will be welcome to all chemists—and they are now many—who require to use mercury in their researches, and who are often more or less incommoded by its impurities.

A subject of still wider interest is the so-called "Mussoenda coffee" of Réunion, which has been examined by Prof. Dunstan and found wanting. It contains neither caffeine nor any similar substance. Still the absence of caffeine would afford no guarantee against the attempt by some enterprising quack to foist the seeds upon the public as an addition to, or a "surrogate" for, coffee. Hence we are very happy to learn on the authority of the British Consul in Réunion that the shrub *Gaertnera vaginata* "yields fewer berries than the coffee tree, and would probably be more expensive."

The investigation of the artificial salicylic acid of commerce by W. R. Dunstan and O. F. C. Bloch will be a useful caution to the medical profession. Commercial salicylic acid (Kolbe's process), whether crude or dialysed, produces different physiological effects from the pure salicylic acid obtained from the oil of winter-green. The best test for the purity of salicylic acid is the determination of its melting-point, which ought to be 156.75°, and its existence in large, separate, well-defined crystals. The question is the more important as one of the ordinary impurities, paracresotic acid, is decidedly poisonous.

We hope that Mr. Dunstan will continue his useful career.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 12, March 20, 1893.

The Minister of Public Instruction has addressed to the Academy an "ampliation" of the decree by which the President of the Republic approves of the election of Sir Joseph Lister as a foreign associate.

Preparation of a Variety of Sprouting Graphite.—Henri Moissan.—Certain natural varieties of graphite if heated in presence of sulphuric acid or a mixture of sulphuric acid and potassium chlorate, assume the curious property of sprouting abundantly if afterwards heated to dull redness upon a plate of platinum. M. Luzi has shown that if these natural graphites are allowed to imbibe a very small quantity of monohydrated nitric acid they swell up on ignition, forming small vermiform or dendritic processes. The cause of the sprouting is the sudden liberation of a small volume of gas expanded by heat.

Researches on Samarium.—Lecoq de Boisbaudran.—The author submits to the Academy the results of a fractionation of Cleve's samaria by means of ammonia. The first fractions were then refractionated with oxalic acid and gave the electric ray $Z\epsilon$ and the reversal band $Z\zeta$; the heaviest band of $Z\beta$ had collected there. The first oxalic deposit is a nearly white earth, which does not show the reversal $Z\beta$; the earth of the tailings which is decidedly yellow gives $Z\beta$. The reversal spectra, Sm and $Z\zeta$, and the electric rays $Z\epsilon$, have approximately the same intensity in the oxalic headings and tailings. I find that $Z\epsilon$ and $Z\zeta$ are more distinct in the ammoniacal headings than in the centre or the tailings. The three bands Sm are also decidedly more marked in the ammoniacal headings than in the centre, which, however, does not contain an appreciable quantity of any earth other than Sm. As far as the indigo of the spectrum, the absorption Sm appears constant in the ammoniacal headings, centres, and tailings. M. Demarçay has undertaken a photographic examination of the absorption in the violet and the ultra-violet. It is remarkable that my prolonged fractionations have not yielded a product giving in HCl $Z\zeta$ decidedly stronger than the orangée Sm. Mr. Crookes has also not obtained his anomalous ray very intense. I think that the band $Z\zeta$ and the anomalous ray are closely related. They are seen with substances rich in Sm, and increase when the three bands of Sm, especially the orange, tend to decrease. In very samariferous yttria, the so-called anomalous ray has the λ indicated by Mr. Crookes. In samariferous gadolinia, lanthana, and terbia, its position varies.

Election of a Correspondent for the Chemical Section vice the late M. Alria.—Sir H. Roscoe obtained 28 votes as against 17 given to Prof. Cannizzaro and 1 to Prof. Mendeleeff, out of a total of 47 votes. Sir H. Roscoe was therefore proclaimed duly elected.

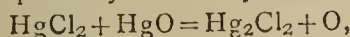
Electric Laboratory Crucible with a Directing-Magnet.—E. Ducretet and L. Lejeune.—This apparatus cannot be intelligibly described without the accompanying cut.

Phenomenon of Dissociation of Sodium Chloride if Heated in Contact with a Septum of Porous Earth.—M. de Sanderval.—If we heat a tube of porous earth in an external atmosphere of sodium chloride in the state of vapour mixed with dry air, the tube becomes filled with chlorine. The exterior atmosphere of sodium chloride contains but little free chlorine. There is here a chemical reaction between the sodium chloride and the silica of the tube and also dissociation by heat. The apparatus is an earthenware tube encased in a wider

porcelain tube, the whole placed in a tube furnace. The sodium chloride is deposited in the annular space between the two tubes, where it is converted into vapour. By leaning the furnace lengthwise we obtain a draught sufficient for introducing the necessary current of air.

Hydurilic and Desoxyamalic Acids.—C. Matignon.—A thermo-chemical paper, not susceptible of useful abstraction, and not of sufficient importance for insertion *in extenso*.

Action of Cotton upon Sublimate absorbed from Dilute Solutions.—Leo Vignon.—The mercury absorbed takes three distinct conditions: one part is soluble in cold water, a second part is soluble in cold acidulated water (10 per cent HCl at 22°), and a third part may be dissolved by boiling solutions of common salt (10 per cent NaCl). From the author's experiments it appears that (1) bleached cotton steeped in dilute solutions of sublimate fixes mercuric oxide in excess in preference to the hydrochloric acid. The fixation may exceed 3(HgO) to 1(HCl). (2) This cotton, if dried at the ordinary temperature and then after some days steeped in water, only gives off a part of its mercury in the state of HgCl₂ and its hydrochloric acid, whilst it retains HgO and Hg₂Cl₂. The calomel is probably formed by the reaction—



the oxygen being absorbed by the cellulose and converting it into oxycellulose. (3) On exposure for some hours to a temperature of 60°, the mercuric chloride and oxide diminish, and the proportion of calomel increases.

The Use of Ruthenium Red in Microscopic Morphology.—Louis Mangin.—The colour discovered by M. Joly in his researches on the ruthenium ammoniacal compounds, rivals the most brilliant coal-tar pigments by its tinctorial intensity. The author has observed that ruthenium red is the best reagent for the pectic compounds, which are always associated with cellulose in young tissues and in old tissues which have not been modified by foreign matters. It is the only reagent for the transformation products of the pectic compounds, *i.e.*, the majority of gums and mucilages.

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Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxi., No. 2.

The Mines and the Metallurgy of Nickel.—All the nickel of commerce is at present obtained from two very extensive deposits,—the one in New Caledonia, and the other at Sudbury, in the province of Ontario, in Canada. The Sudbury ore is remarkable for its freedom from arsenic, and it contains only $\frac{1}{4}$ per cent of cobalt. The nickel ore of New Caledonia is a double nickel and magnesium silicate containing from 8 to 10 per cent of nickel. Its specific gravity is from 2.3 to 2.8, and its colour a pale grey. It contains neither cobalt nor arsenic, and is accompanied by chrome-iron and talc. The Sudbury ore is a sulphide, containing from 2 to 4 per cent of nickel. The fumes given off during the roasting process completely destroy vegetation in the district.

Gold in Finland.—During the eighteen years of working, from 1870 to 1887, the quantity of fine gold obtained has amounted to 321.3 kilos. The sand washed has reached a yearly average of 342 cubic metres.

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Bulletin de la Société Chimique de Paris.
Series 3, Vols. ix. and x., No. 6.

At the meeting of the Society held on March 1, the President announced the new regulations resolved on by the Council concerning "sealed papers," which may, it seems, in some cases lie for twenty-five years unopened, or may be withdrawn by the authors at the end of ten or of twenty years.

Researches on Thallium. New Determination of its Atomic Weight.—Charles Lepierre.—From the *Comptes Rendus*.

A New Oxalylmalonic Diureide.—C. Matignon.—The composition of this substance is expressed by the formula C₇O₆N₄H₆. If heated to 105° it loses 1 mol. of water, and is then apparently anhydrous. It is decomposed by water into barbituric and parabanic acids.

— — —
Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. viii., No. 85.

According to Lindot, phosphoric acid equivalent to 2000 tons calcium phosphate is yearly withdrawn from use and locked up, so to speak, in the cemeteries in the bones of the dead.

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Zeitschrift für Analytische Chemie.
Vol. xxxii., Part 2, 1893.

Gas-Volumetric Determination of Organic Acids and of Iodic Acids.—H. Kux.—This paper does not admit either of abstraction or of full insertion on account of its length and the number of tables which it contains.

Microchemical Detection of Sulphur. Notice on the Use of Gaseous Reagents, especially Bromine Vapour, in Microchemical Analysis.—F. Emich.—This paper will be inserted in full.

Chemico-Legal Examination of Stains suspected to be Blood.—H. Struve.—This paper will be inserted in full.

Iodine Addition Method.—F. Gautter.

New Method for Determining the Iodine-Number in Fats and Oils.—F. Gautter.—Both these papers will be inserted in full.

Determination of Potassium.—E. W. Hilgard.—The weighing of potassium platinum chloride certainly gives good results in experienced hands, especially in the Gooch crucible. Still, the weighing of filters is always a rather critical operation, and may give rise to variable results, according to the experience of the operator and the moisture of the air. I therefore prefer to weigh the reduced platinum, which I effect as follows:—I use a small platinum crucible, reserved exclusively for this use. The inside for about half its height from the bottom, is coated with a layer of platinum sponge, which may be effected in a quarter of an hour by carefully decomposing a few decigrams of the platinum double salt, inclining the crucible sideways and turning it occasionally round. The platinum sponge promotes the decomposition of the double salt so much that it may be quickly and quietly completed at a relatively moderate heat, the cover being kept in its place. When completed, the crucible is heated strongly for some time in order to render the platinum sponge so coherent that on subsequent washing by decantation no traces may rise to the surface and be lost. The chief part of the potassium chloride is volatilised during the last ignition. When cold, two drops of concentrated hydrochloric acid are let fall into the crucible. If on heating there appears the slightest yellowness, the acid is evaporated off and the ignition repeated, adding a little oxalic acid. In the majority of cases the yellowness springs from a trace of ferric chloride, and therefore reappears after the second ignition on the addition of hydrochloric acid. It is then washed by repeated decantation, raising the crucible to ebullition by applying heat to one side. The product is ignited and weighed. The results are nearly always rather lower than those obtained by weighing the double salt, and the acid washings first poured off contains as a rule traces of earths, and almost without exception a little sodium chloride. No correction for the ash of the filter is admissible.

Absorption- and Washing-Apparatus.—C. Mann.—Requires the accompanying illustration.

MEETINGS FOR THE WEEK.

- MONDAY, 17th.—Medical, 8.30.
Society of Arts, 8. "Some Masters of Ornament,"
by Lewis Foreman Day. (Cantor Lectures).
- TUESDAY, 18th.—Institute of Civil Engineers, 8.
Pathological, 8.30.
Royal Institution, 3. "Symbolism in Ceremonies,
Customs, and Art," by John Macdonell, LL.D.
Society of Arts, 8. "The Philippine Islands," by
H. A. McPherson.
- WEDNESDAY, 19th.—Meteorological, 7.
Microscopical, 8.
Society of Arts, 8. "Some Economic Points in
connection with Electricity Supply," by Gis-
bert Kapp.
- THURSDAY, 20th.—Royal, 4.30.
Royal Society Club, 6.30.
Royal Institution, 3. "The Atmosphere," by
Prof. Dewar, F.R.S.
Chemical, 8. "Contribution to the Chemistry and
Physiology of Foliage Leaves," by Horace T.
Brown, F.R.S., and G. Harris Morris, Ph.D.
"The Interaction of Alkali Cellulose and Car-
bon Bisulphide—Cellulose Thio-carbonates," by
C. F. Cross, E. J. Bevan, and C. Beadle. And
other papers.
- FRIDAY, 21st.—Royal Institution, 9. "Possible and Impossible
Economies in the Utilisation of Energy," by Prof.
A. B. W. Kennedy, F.R.S.
Quekett Club, 8.
- SATURDAY, 22nd.—Royal Institution, 3. "Some Applications of
Electricity to Chemistry," by James Swin-
burne, M.Inst.E.E. (The Tyndall Lectures).

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former editions, save that it has been enlarged, and in reality now con-
stitutes a treatise on the chemical substances occurring in the animal
body. As in former editions it is entirely the work of Dr. A. Sheridan
Lea. The references given, though extensive, are not intended to be
exhaustive. An effort has been made to make the references to recent
works as complete as possible, other references are to papers, which
themselves give full references, and will therefore serve as a guide to
literature of the subject; and some have been inserted in order to inform
the student of the dates at which important results were first described."
—From the Preface.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1743.

ON THE DENSITIES OF THE PRINCIPAL GASES.*

By Lord RAYLEIGH, Sec. R.S.

IN former communications (*Roy. Soc. Proc.*, February, 1888; February, 1892) I have described the arrangements by which I determined the ratio of densities of oxygen and hydrogen (15.882). For the purpose of that work it was not necessary to know with precision the actual volume of gas weighed, nor even the pressure at which the containing vessel was filled. But I was desirous before leaving the subject of ascertaining not merely the relative, but also the absolute, densities of the more important gases, that is, of comparing their weights with that of an equal volume of water. To effect this it was necessary to weigh the globe used to contain the gases when charged with water, an operation not quite so simple as at first sight it appears. And, further, in the corresponding work upon the gases, a precise absolute specification is required of the temperature and pressure at which a filling takes place. To render the former weighings available for this purpose, it would be necessary to determine the errors of the barometers then employed. There would, perhaps, be no great difficulty in doing this, but I was of opinion that it would be an improvement to use a manometer in direct connection with the globe, without the intervention of the atmosphere. In the latter manner of working, there is a doubt as to the time required for full establishment of equilibrium of pressure, especially when the passages through the taps are partially obstructed by grease. When the directly connected manometer is employed, there is no temptation to hurry from fear of the entrance of air by diffusion, and, moreover (Note A), the time actually required for the establishment of equilibrium is greatly diminished. With respect to temperature, also, it was thought better to avoid all further questions by surrounding the globe with ice, as in Regnault's original determinations. It is true that this procedure involves a subsequent cleaning and wiping of the globe, by which the errors of weighing are considerably augmented; but as it was not proposed to experiment further with hydrogen, the objection was of less force. In the case of the heavier gases, unsystematic errors of weighing are less to be feared than doubts as to the actual temperature.

In order to secure the unsystematic character of these errors, it is necessary to wash and wipe the working globe after an exhaustion in the same manner as after a filling. The dummy globe (of equal external volume, as required in Regnault's method of weighing gases) need not be wiped merely to secure symmetry, but it was thought desirable to do so before each weighing. In this way there would be no tendency to a progressive change. In wiping the globes the utmost care is required to avoid removing any loosely attached grease in the neighbourhood of the tap. The results to be given later will show that, whether the working globe be full or empty, the relative weights of the two globes can usually be recovered to an accuracy of about 0.3 m.grm. As in the former papers, the results were usually calculated by comparison of each "full" weight with the mean of the immediately preceding and following empty weights. The balance and the arrangements for weighing remained as already described.

The Manometer.

The arrangements adopted for the measurement of pressure must be described in some detail, as they offer

several points of novelty. The apparatus actually used would, indeed, be more accurately spoken of as a manometric gauge, but it would be easy so to modify it as to fit it for measurements extending over a small range.

The object in view was to avoid certain defects to which ordinary barometers are liable, when applied to absolute

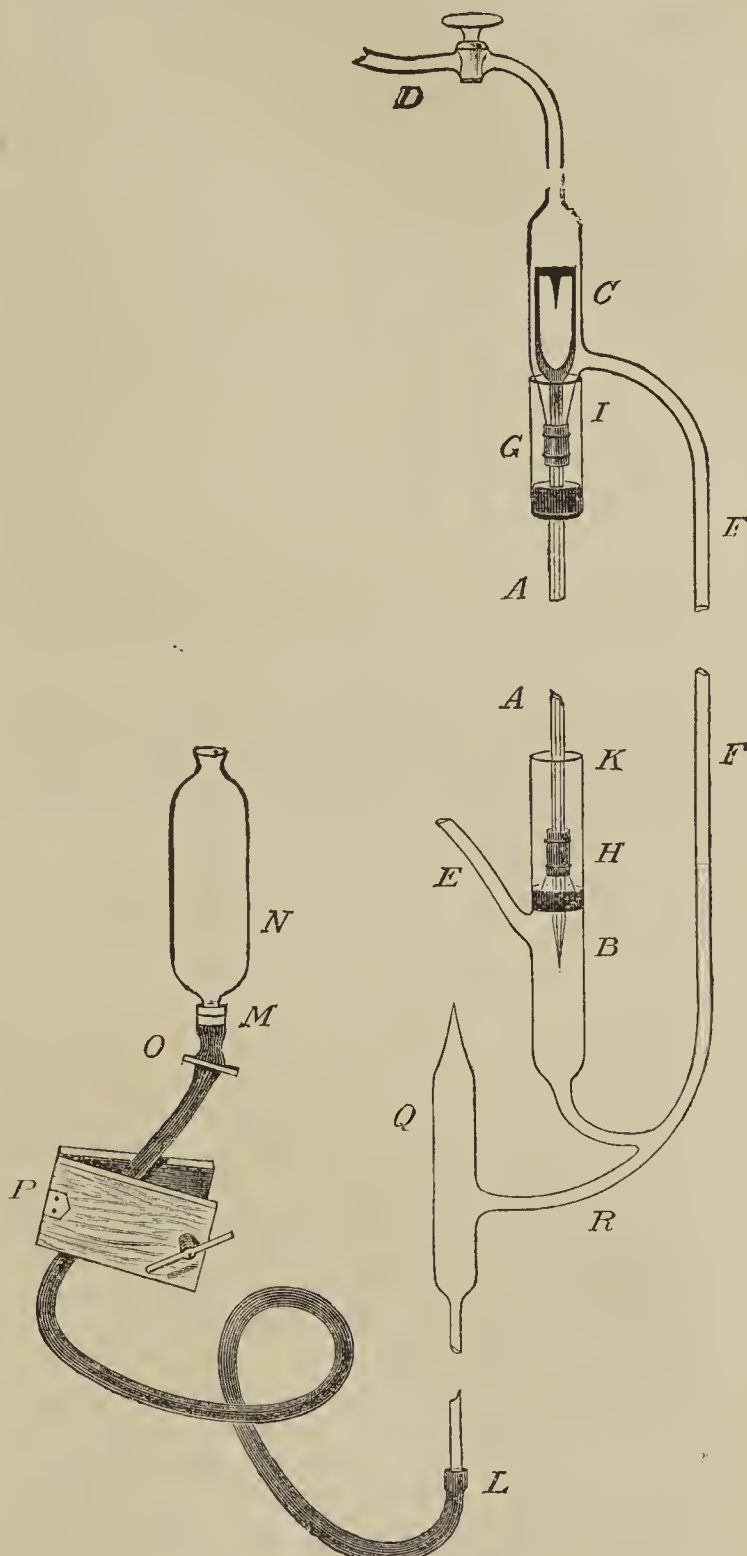


FIG. 1.

measurements. Of these three especially may be formulated:—

- It is difficult to be sure that the vacuum at the top of the mercury is suitable for the purpose.
- No measurements of a length can be regarded as satisfactory in which different methods of reading are used for the two extremities.
- There is necessarily some uncertainty due to irregular refraction by the walls of the tube. The apparent level of the mercury may deviate from the real position.

* A Paper read before the Royal Society.

d. To the above may be added that the accurate observation of the barometer, as used by Regnault and most of his successors, requires the use of a cathetometer, and expensive and not always satisfactory instrument.

The guiding idea of the present apparatus is the actual application of a measuring rod to the upper and lower mercury surfaces, arranged so as to be vertically superposed. The rod AA, Fig. 1, is of iron (7 m.m. in diameter), pointed below B. At the upper end, C, it divides at the level of the mercury into a sort of fork, and terminates in a point similar to that at B, and, like it, directed downwards. The coincidence of these points with their images reflected in the mercury surfaces, is observed with the aid of lenses of about 30 m.m. focus, held in position upon the wooden framework of the apparatus. It is, of course, independent of any irregular refraction which the tube may exercise. The verticality of the line joining the points is tested without difficulty by a plumb-line.

The upper and lower chambers, C, B, are formed from tubing of the same diameter (about 21 m.m. internal). The upper communicates through a tap, D, with the Töpler, by means of which a suitable vacuum can at any time be established and tested. In ordinary use, D stands permanently open, but its introduction was found useful in the preliminary arrangements and in testing for leaks. The connection between the lower chamber B and the vessel in which the pressure is to be verified takes place through a side tube, E.

The greater part of the column of mercury to which the pressure is due is contained in the connecting tube, FF, of about 3 m.m. internal diameter. The temperature is taken by a thermometer whose bulb is situated near the middle of FF. Towards the close of operations the more sensitive parts are protected by a packing of tow or cotton-wool, held in position between two wooden boards. The anterior board is provided with a suitable glass window, through which the thermometer may be read.

It is an essential requirement of a manometer on the present plan that the measuring rod pass air-tight from the upper and lower chambers into the atmosphere. To effect this the glass tubing is drawn out until its internal diameter is not much greater than that of the rod. The joints are then made by short lengths of thick walled indiarubber, H G, wired on and drowned externally in mercury. The vessels for holding the mercury are shown at I K. There is usually no difficulty at all in making perfectly tight joints between glass and tubes in this manner; but in the present case some trouble was experienced in consequence apparently of the imperfect approximation between the *iron* and the mercury. At one time it was found necessary to supplement the mercury with vaseline. When tightness is once obtained, there seems to be no tendency to deterioration, and the condition of things is under constant observation by means of the Töpler.

The distance between the points of the rod is determined under microscopes by comparison with a standard scale, before the apparatus is put together. As the rod is held only by the rubber connections, there is no fear of its length being altered by stress.

The adjustment of the mercury (distilled in a vacuum) to the right level is effected by means of the tube of black rubber, LM, terminating in the reservoir, N. When the supply of mercury to the manometer is a little short of what is needed, the connection with the reservoir is cut off by a pinch-cock at O, and the fine adjustment is continued by squeezing the tube at P between a pair of hinged boards, gradually approximated by a screw. This plan, though apparently rough, worked perfectly, leaving nothing to be desired.

It remains to explain the object of the vessel shown at Q. In the early trials, when the rubber tube was connected directly to R, the gradual fouling of the mercury surface, which it seems impossible to avoid, threatened to interfere with the setting at B. By means of Q, the mer-

cury can be discharged from the measuring chambers, and a fresh surface constituted at B as well as at C.

The manometer above described was constructed by my assistant, Mr. Gordon, at a nominal cost for materials; and it is thought that the same principle may be applied with advantage in other investigations. In cases where a certain latitude in respect of pressure is necessary, the measuring rod might be constructed in two portions, sliding upon one another. Probably a range of a few millimetres could be obtained without interfering with the indiarubber connections.

The length of the iron rod was obtained by comparison under microscopes with a standard bar, R, divided into millimetres. In terms of R the length at 15° C. is 762.248 millimetres. It remains to reduce to standard millimetres. Mr. Chaney has been good enough to make a comparison between R and the iridio-platinum standard metre, 1890, of the Board of Trade. From this it appears that the metre bar R is at 15° C. 0.3454 m.m. too long; so that the true distance between the measuring points of the iron rod is at 15° C.—

$$762.248 \times 1.0003454 = 762.511 \text{ m.m.}$$

Connections with Pump and Manometer.

Some of the details of the process of filling the globe with gas under standard conditions will be best described later under the head of the particular gas; but the general arrangement and the connections with the pump and the manometer are common to all. They are sketched in Fig. 2, in which S represents the globe, T the inverted

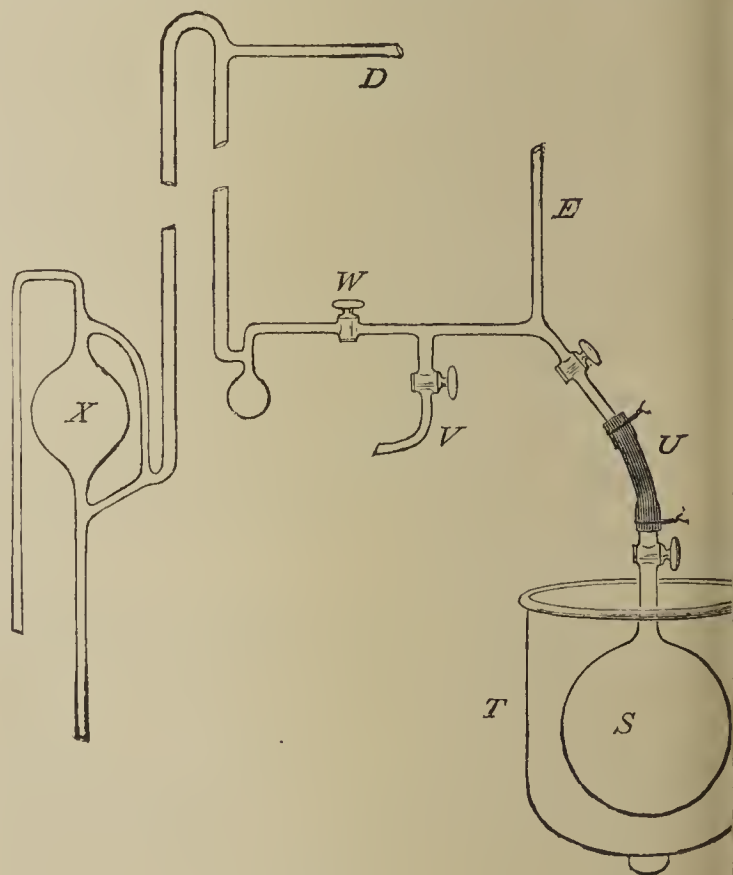


FIG. 2.

bell-glass employed to contain the enveloping ice. The connection with the rest of the apparatus is by a short tube, U, of thick rubber, carefully wired on. The tightness of these joints was always tested with the aid of the Töpler, X, the tap, V, leading to the gas generating apparatus being closed. The side tube at D leads to the vacuum chamber of the manometer, while that at E leads to the pressure chamber, B. The wash out of the tubes, and in some cases of the generator, was aided by the Töpler. When this operation was judged to be complete, V was again closed, and a good vacuum made in

the parts still connected to the pump. w would then be closed, and the actual filling commenced by opening v, and finally the tap of the globe. The lower chamber of the manometer was now in connection with the globe, and through a regulating tap (not shown) with the gas-generating apparatus. By means of the Töppler, the vacuum in the manometer could be carried to any desired point. But with respect to this a remark must be made. It is a feature of the method employed (due to von Jolly) that the exhaustions of the globe are carried to such a point that the weight of the residual gas may be neglected, thus eliminating errors due to a second manometer reading. There is no difficulty in attaining this result, but the delicacy of the Töppler employed as a gauge is so great that the residual gas still admits of tolerably accurate measurement. Now in exhausting the head of the manometer it would be easy to carry the process to a point much in excess of what is necessary in the case of the globe, but there is evidently no advantage in so doing. The best results will be obtained by carrying both exhaustions to the same degree of perfection.

At the close of the filling the pressure has to be adjusted to an exact value, and it might appear that the double adjustment required (of pressure and of mercury) would be troublesome. Such was not found to be the case. After a little practice the manometer could be set satisfactorily without too great a delay. When the pressure was nearly sufficient, the regulating tap was closed, and equilibrium allowed to establish itself. If more gas was then required, the tap could be opened momentarily. The later adjustments were effected by the application of heat or cold to parts of the connecting tubes. At the close, advantage was taken of the gradual rise in the temperature which was usually met with. The pressure being just short of what was required, and v being closed, it was only necessary to wait until the point was reached. In no case was a reading considered satisfactory when the pressure was changing at other than a very slow rate. It is believed that the comparison between the state of things at the top and at the bottom of the manometer could be effected with very great accuracy, and this is all that the method requires. At the moment when the pressure was judged to be right, the tap of the globe was turned, and the temperature of the manometer was read. The vacuum was then verified by the Töppler.

(To be continued).

DETERMINATION OF THE ALKALIS IN SILICATES.

By ALBERT H. LOW.

THE following scheme is given more as a suggestion than as a description of a well-established method. The author had occasion to make some alkali determinations in a hurry, without great regard to extreme accuracy. J. Lawrence Smith's method was out of the question, as all the carbonate of calcium at hand was too impure to be available. A consideration of the fact that in the author's method for zinc (described in the *Journal of Analytical and Applied Chemistry*, Sept., 1892) all the zinc is extracted from a dried residue containing the substances from which it is ordinarily difficult to effect a good separation, led to the idea that a similar scheme might be as successfully applied to the case of the alkalis. The following method was then devised and tried with satisfactory results. If the bulks of the various filtrates, &c., are kept as small as possible, and the evaporations conducted with care over direct heat, the time required is considerably less than for Smith's method.

Treat one grm. of the finely-powdered silicate by warming gently with pure strong hydrofluoric acid and a little sulphuric acid in a 100 c.c. platinum dish until decomposition is complete. Evaporate to dryness, and heat

until the fumes of sulphuric acid have nearly ceased coming off. Cool, and add a little ammonia water, and boil. See that a good disintegration is effected. Filter, washing with a little hot water. Acidify the filtrate strongly with hydrochloric acid, and add as small an excess as practicable of chloride of barium solution. Heat to boiling and filter, washing with hot water. Evaporate the filtrate to dryness in platinum, and ignite gently to expel ammonium salts. Cool, add a little carbonate of ammonium and ammonia water, boil, and filter, washing with hot water. Evaporate the filtrate to dryness in a weighed platinum dish. This gives the combined chlorides which are separated in the usual manner.

As the author had but little time to investigate as to the accuracy of this method, he sent a description to Dr. W. F. Hillebrand, of the U.S. Geological Survey at Washington, with the request that it be compared with the method in use. Dr. Hillebrand kindly complied and sent the following figures as the results of his analyses of two different samples of rock:—

	No. I. Per cent.		No. II. Per cent.	
	K ₂ O.	Na ₂ O.	K ₂ O.	Na ₂ O.
Smith's method	1'95	4'09	0'32	3'53
Low's ,,	1'91	4'10	0'35	3'55

Dr. Hillebrand suggests that his results by Low's method may be a trifle high, owing to the presence of a trace of potassium permanganate in his hydrofluoric acid, and, on the other hand, a trifle low from the retention of alkali by magnesia, the two errors counterbalancing. Pure hydrofluoric acid is, however, easily obtained, and the error due to magnesia might possibly be avoided by using carbonate of ammonium in the original extraction. *Journal of Analytical and Applied Chemistry*, vi., No. 12.

ON THE PURIFICATION OF WATER USED FOR STEAM-BOILERS.*

By R. JONES, Ph.D.

(Concluded from p. 173).

THE following example illustrates the use of carbonate of soda for the purpose of water purification. A boiler under my supervision is fed with water from the Elbe, treated by warming with carbonate of soda solution and passing through a filter-press. Our system is neither Dehne's, nor Klein, Schanzlin, and Becker's. A filter-press that had formerly been used for a different purpose was unearthed and requisitioned, and for a warming-vessel we made use of a small steam-boiler, for which we had no other use. The apparatus was put together by our own workmen, the only cash expended being twelve marks for a small graduated cock obtained from Klein, Schanzlin, and Becker's for regulating the flow of the soda solution. The apparatus, notwithstanding its cheapness, works to our complete satisfaction, and a similar one could easily be fitted up in any other works. The consumption of carbonate of soda amounts to 2.5 kilos. a day. We add just so much solution as suffices after filtration to produce a distinct red colour with phenolphthalein, a solution of which the boiler attendant has always ready at hand. A sample, however, is examined every day in the laboratory, and the mere depth of colour produced by adding phenolphthalein is sufficient to denote if the correct quantity of soda has been used. For two weeks we made a determination daily of the excess of soda by titration with sulphuric acid, using phenolphthalein as indicator, and found per litre 0.046, 0.031, 0.031, 0.138, 0.092, 0.046, 0.183, 0.031, 0.153, 0.198, 0.046,

* From the *Zeit. Angew. Chemie*, 1892, p. 15.—Communicated by H. H. B. Shepherd.

0.122 grm. carbonate in excess. These figures are taken from our actual working of the process, and they show that an ordinary boilerman is quite able to master the work required. The boiler was worked day and night uninterruptedly for thirteen weeks, and blown off every day from the highest to the lowest water level. When laid off there was a trifling quantity of sludge in the boiler, and in a part of the tubes a deposit of sulphate of lime of about the thickness of a sheet of paper; this, however, was easily scraped off. The following analyses by Dr. Farnsteiner show the composition of the water used:—

	Grms. per 100 litres.	
	Before Purification.	After Purification.
Residue	32.0	37.9
Lime	4.7	1.1
Magnesia	1.3	1.0
Sulphuric acid	3.5	3.5
Silicic acid	1.1	1.1
Sodium chloride.. . . .	16.7	16.1
„ carbonate	—	13.8
Combined carbonic acid . .	3.3	—
	30.6	36.6

My own analysis of the water taken from the boiler at the end of the thirteen weeks was as follows:—

Grms. per 100 litres.	
Residue.. . . .	751.7
Silicic acid	0.7
Magnesium sulphate . . .	2.5
Calcium sulphate	17.3
Sodium sulphate.. . . .	107.2
„ carbonate	12.2
„ chloride	581.6
Oxide of iron	1.8
	723.3

The analysis of the sludge was as follows:—

Insoluble matter.. . . .	10.00
Calcium carbonate	55.86
„ sulphate	4.87
Magnesia hydrate	21.74
Oxide of iron	7.53
	100.00

The sludge gave only a dark green colour with potassium ferricyanide.

The result does not at the first glance seem very satisfactory, since only three-fourths of the lime and practically none of the magnesia was precipitated. If, however, we consider the ultimate result—the analysis of the water remaining in the boiler at the end of the period and the interior condition of the boiler—we see how the excess of soda by concentration has caused the almost complete separation of the salts which cause incrustation.

We have now to consider the effect of supplementing the carbonate of soda either by caustic soda, as used by Dehne, or by quicklime as used by Dervaux. As neither, however, effects a more complete precipitation of the lime than carbonate of soda does alone, they offer no advantage from the point of view of hindering the formation of sulphate of lime deposits. It is true a more complete separation of magnesia is possible by their use, but this in our case is superfluous, since carbonate of soda alone is sufficient to keep the magnesia within bounds.

Dehne makes it a special point that water treated by his method will indicate 0° of hardness. A chemist working in his laboratory can, of course, remove every-

thing capable of being precipitated without using an appreciable excess of reagents; an ordinary boilerman, however, could scarcely accomplish this feat, and to attempt to compile from the results of a single analysis a code of directions once for all, is, from a chemist's point of view, inadmissible. Dehne's system also (at any rate as far as the chemical part of it is concerned), necessitates a knowledge of the "negative hardness" of the water, *i.e.*, the percentage of magnesia. This is needful in order to insure the removal of the excess of caustic soda, without which the promised results are not obtainable. Many instances could be given of the evil effect of such an excess. For example, the board of management of the local quay (Hamburg), finding the river water too impure for their boiler, sank a well to obtain another supply. This well-water, however, proved to be variable in composition, and not at all suitable for the purpose. A sample was found by Wibel to contain per 100,000 parts:—

Calcium carbonate . . .	23.2
Calcium sulphate . . .	60.0
Magnesium sulphate . .	18.0

The water was purified by Dehne's method with a mixture of caustic and carbonate of soda with the result that after a short time the boiler became useless. According to the official report, the use of too large a quantity of caustic soda had caused its ruin. A deeper well now supplies an excellent water, free from gypsum, and containing 14.1 parts calcium carbonate and 1.6 parts magnesium carbonate per 100,000, and Dehne's system is given up.

An analogous case is reported by Münter, of Halle. This likewise concerns newly erected boilers fed with water purified by caustic and carbonate of soda. The boiler plates became corroded, and an analysis of the water revealed the presence of sulphate of soda and sufficient oxide of iron to colour the water red. A somewhat similar experience is reported by Abel, of Frankfurt.

This all tends to show the undesirability of regarding the subject of water purification as an engineer's question only, and indicates that its importance is sufficient to demand a greater influence on the part of the chemist. The services rendered by our boiler inspection societies with their staffs of engineers are certainly, as far as they go, admirable, but with chemical questions they are less competent to deal, and if owners of works had the advantage of a chemical as well as a technical adviser always at hand, such frauds as those of the anti-incrustator nostrums could not be carried to such a pitch.

Two important advantages are gained by the use of carbonate of soda alone, which are lost if caustic soda (or what, chemically speaking, is the same thing, caustic lime and carbonate of soda) be substituted:—

1. The easy control over the use of the reagents, and consequent avoidance of either too large or too small a quantity.

2. The knowledge that some excess, if not of unusual proportions, does no harm.

The advantage gained by the use of caustic soda in exchange for the above is, as has already been shown, a pure illusion.

Were it possible, however, to reach Dehne's ideal, and to obtain a water showing 0° hardness and no negative hardness, it would still be undesirable to do so; for, according to Burgdoff, unless some sludge is deposited in a boiler it does not remain tight.

For the rest it is quite easy to assure one's self that the excess of carbonate of soda in the boiler water is not too large. All that is necessary is to draw off a little water from time to time, and notice if it gives a large precipitate with a solution of calcium sulphate,—a test any boilerman is capable of making; or phenolphthalein may be used, in which case the indication is conveyed by the colour imparted to the water.

Langfurth recommends, as a preventive against boiler incrustation without the use of chemicals, the plan o

blowing off the water as soon as the concentration has reached the point at which gypsum begins to separate out,—a plan which has been used successfully with locomotive boilers.

An indirect means of diminishing the formation of incrustation consists in condensing the exhaust steam and using it for feed water, and apparatus have been constructed for this purpose by Klein, Schanzlin, and Becker. The plan can be recommended in cases where the lubricating oils are exclusively mineral; with animal or vegetable oils, however, it is open to very grave suspicion, as fatty acids are sure to be formed in the boiler, which not only of themselves cause corrosion, but form combinations with the lime and magnesia salts, giving rise to incrustation of a very malignant description.

In conclusion, a few words concerning the many bogus anti-incrustator compounds, which are continually being pressed upon the public under most seductive appellations. A determined crusade, not altogether destitute of results, was fought against them by the Heiz experimental station in Karlsruhe. These nostrums have but one action in common which can be relied upon: they fill the pockets of the vendors so long as fools are forthcoming to be victimised. In other respects they are mostly either useless or else positively harmful, whilst the few that are really compounded with a view to efficiency are offered at three or four times their actual value, sometimes even more.

A METHOD FOR DETERMINING THALLIUM BY TITRATION.

By K. SPONHOLZ.

In a neutral or acid solution a thalious salt may be converted by bromine-water into a corresponding thallic salt. The oxidation is instantaneous, and as its end is shown with sufficient precision by the liquid turning yellow, this reaction may be used for the quantitative determination of thallium. Two atoms of bromine correspond to one atom of thallium. For instance, for 0.2176 gm. $\text{TlNO}_3 = 0.1669$ gm. Tl there were used 10.5 c.c. bromine water, containing per c.c. 0.01244 gm. bromine. Consequently, 0.0008175 atom Tl represents 0.001635 atom bromine, or 1 atom $\text{Tl} = 2$ atoms bromine.

Thallium weighed (as TlNO_3).	Thallium found.
0.4894 gm.	Mean 0.4890
0.1669 „	„ 0.1666
0.0166 „	„ 0.0159

For effecting the titration we prepare a 1.6th normal bromine-water (for determining larger quantities a more concentrated solution may be used) by means of potassium iodide and sodium thiosulphate. The point of a burette, graduated in 1.10th c.c., is plunged into the acid solution of thallium, and the bromine is allowed to flow in until the excess of bromine causes a distinct yellowness of the thallium solution to appear. The immersion of the point of the burette is necessary, as otherwise the determination is rendered inaccurate by the evaporation of the bromine. The liquid must also be acidified, as thallic salts are decomposed by water, and after the separation of the dark coloured thallium hydroxide the end of the reaction cannot be distinctly recognised. As a correction, the quantity of bromine is determined which gives a distinct yellow colour to a volume of water equal to the thallium solution. It is trifling, but it occasions slight deviations from the mean values.

The standard of the bromine solution must be re-determined each time when the burette is filled, which may be effected expeditiously by means of the method with potassium iodide and sodium thiosulphate. In consequence of the rapid evaporation of the bromine, the

titration must be effected at once, and it is well to use only the first 30 to 35 c.c. of a burette holding 50 c.c. Or the standard may be determined both before and after the titration.—*Zeit. Anal. Chemie.*

PHYSICAL PROPERTIES OF MELTED RUTHENIUM.

By A. JOLY.

OF the six metals forming the platinum group there are three (platinum, iridium, and palladium) the physical properties of which have been more particularly examined by H. Sainte-Claire Deville and Debray. I purpose completing the study of the metals of the groups as regards the three rarer metals, rhodium, osmium, and ruthenium.

This study has become possible for ruthenium in particular, of which I have prepared 3 kilos. in a state of purity. Further, thanks to the inexhaustible kindness of Mr. G. Matthey, I am at present operating on some 50 kilos. of residues from the preparation of iridium, which will enable me to obtain by a new method 10 kilos. of this rare metal. In order to bring the metal into a state comparable to that of the other platinum metals, I intend melting it in a large mass.

Ruthenium is, along with osmium, the most refractory of the platinum metals. Deville and Debray have only with much difficulty succeeded in melting some small globules with the oxyhydrogen blowpipe. During this operation we are incommoded by the oxidisability of the metal, which tends to be transformed into the volatile oxide RuO_4 . It was evident *a priori* that one might easily succeed with the electric arc. With the electric installation at my disposal, I was able to fuse small globules of from 1 to 2 grms. The particles thus obtained have been melted into reguli of from 25 to 30 grms.—thanks to the kindness of M. de Neville, who placed a more powerful arc at my disposal.

By means of raising the metal suddenly to a temperature much above its melting-point, the fusion is effected in a few moments, and the loss by volatilisation is scarcely sensible. We scarcely perceive the characteristic odour of the peroxide, but whilst cooling it becomes covered with the blue bioxide. After remaining for a few moments in aqua regia, which attacks neither the metal nor the oxide, then in hydrofluoric acid, and a final reduction in hydrogen, the metal is laid bare. By its grey colour it approximates to iron rather than platinum. Its structure is crystalline, and hence it is brittle in the cold. If heated to redness in the flame of the oxyhydrogen blowpipe it may be flattened out and then breaks. Further, the metal spirits strongly at the moment of solidification, and the globules are almost always full of cavities.

The specific gravity of the metal melted and pulverised is at 0° , and referred to water at $4^\circ = 12.063$, the metal being the same which had served for the determination of the atomic weight (*Comptes Rendus*, cviii., 946). For the same sample not fused M. Violle found the specific gravity 12.002. In same apparatus and under the same conditions of temperature, the fusion of ruthenium is more difficult than that of rhodium, which, in turn, is melted with rather more difficulty than platinum; it is remarkably harder to melt than iridium (1950°).

As for the exact melting-point, M. Violle, whose beautiful researches on the measurement of high temperatures are well known, has undertaken its determination. In the conditions at which ruthenium melts, osmium is merely agglomerated and fritted. Iridium osmide, which cannot be melted with the oxyhydrogen blowpipe, is melted with great difficulty into a white crystalline mass, which the best tempered tools do not succeed in cutting.—*Comptes Rendus*, cxvi., p. 430.

DETERMINATION OF FLUORINE IN
COMBUSTIBLE GASES.

By MAURICE MESLANS.

ORGANIC fluorides are in general very stable; the hydrofluoric ethers especially are decomposed only under the action of an elevated temperature, and when the compounds are gaseous the determination of the fluorine presents some difficulties.

The following method appears to furnish at once the most accurate and expeditious results:—

When the combustible organic fluorides are burnt in oxygen, the fluorine is entirely transformed into hydrofluoric acid if the molecule contains the quantity of hydrogen necessary for this transformation. We may then either perform a volumetric determination of this acid by means of an alkaline solution, or convert it into calcium fluoride and thus weigh the fluorine.

In each case the apparatus is composed of a glass combustion-flask, holding about 500 c.c., and closed with a caoutchouc stopper pierced with three holes. One of these gives passage to a glass cock, in which is cemented a tube of platinum, descending to the centre of the flask. The two others give passage to two glass tubes, in which two thick platinum tubes are cemented. Within the flask one of the wires is in contact with the platinum tube, the other descends parallel to it. A finer platinum wire is coiled round the platinum tube, and its spirals are continued in the direction of its prolongation, forming thus an open tube, the extremity of which is fixed upon the second conductor. The spiral can be raised to incandescence by means of an electric current.

Volumetric Determination.—We place in the flask a known volume of a dilute standard solution of potassa, we form a vacuum in it by means of a water air-pump, and we introduce about 400 c.c. of oxygen; a partial vacuum (about 10 c.m. of mercury) is preserved in the flask.

The gas to be analysed is measured over mercury into a bell graduated and fitted with a cock; a caoutchouc tube connects the bell to the flask. By manipulating the cocks, the gas is caused to pass slowly from the bell into the flask. As it issues from the platinum tube it meets the incandescent spiral and is at once ignited. Whilst holding the tube in the hand with its neck almost horizontal, we give it a movement which turns the liquid to the interior and causes it continually to moisten the sides; the hydrofluoric acid formed by the combustion is immediately absorbed by the alkaline liquid and the glass is not attacked. When the bell is filled with mercury we close the cock for a moment, and after having introduced a few c.c. of air we open the cock again to drive into the flask the gas contained in the tube. It is then merely necessary to titrate the liquid in order to find the weight of the hydrofluoric acid absorbed.

Determination in the State of Calcium Fluoride.—To determine the fluorine by weight we operate in the same manner, but substitute for the standard alkaline liquid a pure milk of lime. After the combustion, the flask contains a mixture of lime and of calcium carbonate and fluoride. This mixture is poured into a platinum capsule in which we collect the washing-waters; after evaporation on the water-bath we ignite to render the calcium fluoride easy to filter. It is re-dissolved in acetic acid and evaporated to dryness on the water-bath. After having exhausted the residue with boiling water, we filter, ignite, and weigh the calcium fluoride.

If we wish to operate upon a very large volume of gas we may do it without increasing the bulk of the combustion-flask. It is sufficient to substitute for the simple cock a 3-way cock connected by its third branch with a receiver of oxygen. The products of combustion being entirely absorbed by the reagent, a vacuum is produced in the flask by the combustion itself, and to continue the operation it is merely necessary to introduce a new charge of oxygen.—*Bull. Soc. Chim. de Paris*, vols. ix.—x., No. 4, p. 109.

THE PHOTOGRAPHIC PROPERTIES OF THE
CERIUM SALTS.

By MM. AUGUSTE and LOUIS LUMIÈRE.

WE know that cerium yields two principal series of salts. The former are very stable, whilst the ceric salts are brought back to the lower stage of oxidation even by feeble reducing agents. Some among them, more especially the organic salts, are even reduced spontaneously as soon as formed, so that hitherto it has not been found possible to isolate them.

The easy reductibility of the ceric salts has led us to study the action of light upon these substances, and we have been able to observe that this action effects a rapid reduction which may serve as a basis for the establishment of interesting photographic procedures.

Among the mineral salts which have yielded us the best results we may mention ceric sulphate and nitrate obtained by dissolving ceric hydroxide in sulphuric or nitric acids. The aqueous solutions of these salts have served to saturate sheets of paper, suitably sized and coated with a thin layer of gelatin, which the cerium salt colours an intense yellow. After drying in the dark, the papers were exposed to light under a positive proof. In all the transparent parts the luminous rays reduce the ceric salt to the cerous state, and the paper is decolorised at these parts. This progressive decoloration enables us to follow the action of the light and to stop the impression at the proper moment.

The proof when thus obtained must be treated with a reagent capable of differentiating the cerous from the ceric salt, so as to accentuate and fix the image. In an analogous process with the manganic salts, which we have formerly published (*Bulletin de la Soc. Française de Photographie*, p. 218, 1892), we used the striking oxidising properties of the manganic salts to form insoluble colouring matters with a great number of substances of the aromatic series. In the same manner, if we treat the proofs with cerium salts with these reagents we form and fix colouring matters at the points where the ceric salt has not been reduced by the light. It then suffices to eliminate, by washing, the excess of the reagent as well as the cerous salt to obtain a proof distinctly fixed. It is important that the colouring substance produced should be insoluble, so that it may not be carried away by the washing.

We found, on considering their photographic utilisation, and on comparing the action of the ferric, cobaltic, manganic, and ceric salts upon a great number of substances of the aromatic series, that the ceric salts are capable of yielding coloured reactions much more numerous than the salts of the other metals.

Among the most characteristic reactions we may mention the following:—

In an acid solution the proofs are grey with phenol, green with aniline salts, blue with naphthylamine α , brown with amido-benzoic acid, red with parasulphanilic acid, green with the salts of orthotoluidine, &c. On treatment with ammonia the colour changes; it becomes, for instance, violet with aniline, red with methylamine, &c.

Photographic papers prepared with cerium salts possess a much greater sensitiveness than that of the preparations with ferric or manganic salts.—*Comptes Rendus*, cxvi., p. 574.

Detection of Ammonia with the Nessler Test.—L. L. de Koninck.—In ammoniacal solutions the Nessler test does not produce the usual yellowish-brown precipitate in presence of alcohol, nor even a colouration. The reaction of ammonia with mercuric chloride (Bohlig's test) is not prevented by alcohol.—*Zeitschrift Analytische Chemie*, Part 2, 1893.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 16th, 1893.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MESSRS. Edgar E. Horvill and Edward Brooke were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Ralph Edward Brown, Perranporth, Truro, Cornwall; William Robert Burnett, Wiesbaden, Rollupitiga Road, Colombo, Ceylon; Joshua Buchanan, 63, West Cumberland Street, Glasgow; Robert Cecil T. Evans, Swan's Nest, Stratford-on-Avon; Sorabji Manekji Kaka, M.R.C.S., Karachi, Sind, India; Raffaello Nasini, Padua; John Wilkinson, Gas Works, Drighlington, Yorks.

Of the following papers those marked * were read:—

*131. "*The Limits of Accuracy of Gold Bullion Assaying, and the Losses of Gold Incidental to it.*" By T. K. ROSE.

Some of the causes of the errors in the assay of gold bullion by the ordinary method are referred to, and it is shown that—

1. A higher degree of accuracy is attained if the weighings be made with the precautions recommended by Kohlrausch and others on a balance indicating differences of 0.01 per 1000 ($\frac{1}{2}$ grm.), instead of 0.05 per 1000, which is the smallest difference shown on ordinary assay balances.

2. Differences either in the amount of copper present to the extent of only 16 parts per 1000 of alloy, or in the amount of silver added to the extent of 3 per cent, produce alterations in the "surcharge" of about 0.05 and 0.1 per 1000 respectively, the "surcharge" being the difference in weight between the gold existent in the assay piece originally taken and the cornet finally obtained; it is the algebraical sum of the gold lost and the silver remaining undissolved by the acids. The reduction in the surcharge due to the presence of antimony, zinc, tellurium, iron, or nickel is also given.

It therefore follows that, in order to ensure accuracy, check assays must be made on alloys of the same composition as those under examination.

3. The want of uniformity of temperature ordinarily prevailing in the muffle furnace during cupellation causes variations in the surcharge. The temperatures of the different parts of a muffle at the Royal Mint were taken during cupellation by a thermoelectric pyrometer—consisting of a platinum and rhodioplatinum couple—on three occasions, from which it appears that the mean temperature of the muffle was 1063.7°. At this temperature a rise of about 5° is found to be accompanied by a reduction in the surcharge of about 0.01 per 1000.

If attention be paid to these points, the gold in bullion of a high degree of purity can be determined within a range of ± 0.02 per 1000, the limits of accuracy having been previously considered to be ± 0.10 per 1000. This extreme degree of accuracy is only possible if the check gold be pure.

In the second part of the paper the losses of gold in bullion assaying are estimated. They are due to (1) absorption by the cupel; (2) volatilisation in the muffle; (3) dissolution in the parting acid.

The results of a number of assays are given, the gold having been in each case recovered from the cupels and acids, and, after the gold so recovered has been allowed for, the loss by volatilisation is estimated by difference. The losses, in parts per 1000, observed in the assay of standard gold (916.6 fine) were as in accompanying Table.

A and B are means of four, and C a mean of three, determinations. Other results are also given.

The determination of the amount of gold volatilised is only approximate, as the result obtained represents the

	A.	B.	C.
In cupel	0.513	0.36	0.51
,, first acid	?	0.01	0.03
,, second acid	0.012	0.02	0.04
Volatilised	0.075	0.05	0.06
Total loss	0.600	0.44	0.64

algebraical sum of the errors in several estimations added to the true amount. However, it probably usually lies between 0.5 and 0.1 per 1000.

*132. "*The Volatilisation of Gold.*" By T. K. ROSE.

The loss of gold involved in the fusion of the pure metal and its alloys was investigated by subjecting small test pieces of from 0.5 to 2 grms. in weight to a high temperature under varying conditions on bone-ash cupels placed in a muffle. The work may be considered to be a continuation of the researches of James Napier (*J. Chem. Soc.*, x., 229; xi., 171). The temperatures varied from 1045° to 1300°, and were measured by either a platinum and rhodioplatinum couple or the optical pyrometer devised by M. le Chatelier. The losses of gold could not be measured by the alteration of the mass of the test pieces in the muffle owing to absorption of gases, which sensibly augment the weight of the gold buttons. The true loss was found by assaying the buttons after fusion.

A considerable number of results are quoted. The chief points of interest to which attention is drawn are that:—

1. An increase in the loss of gold takes place when the temperature is high, pure gold losing four times as much at 1245° as at 1090°.

2. A large amount of gold is volatilised in an atmosphere mainly consisting of carbonic oxide, while a small amount is lost in coal gas.

3. A comparatively small amount of gold is carried away by the more volatile metals, copper appearing to exert an exceptional action; metals which are easily volatilised do not appear to be completely driven off by the highest temperatures attained in the experiments.

4. A large proportion of gold is lost in the case of alloys which form flat buttons on the cupel, and, conversely, a small proportion is lost from spherical ones, although the surface actually exposed is greater in the latter case than in the former. A current of air or gas passing over the buttons does not seem to increase the loss, provided the surface of the molten metal remain at rest. These results point to the conclusion that the conditions which lower the surface tension of the gold button simultaneously raise the vapour pressure of the gold.

DISCUSSION.

Professor ROBERTS-AUSTEN said that, prior to the last few weeks, he should certainly have considered that the accuracy of an assay of gold was comprised within a range of $\pm 2/10,000$. Mr. Rose had, however, tracked the errors to their respective sources, and had shown that a still higher degree of accuracy can be attained in ordinary work. It was not a little remarkable that although Princep (one of the best Assay Masters who ever held that important office) had clearly indicated in 1827 the importance of knowing the variations of temperature in an assay muffle, no one had attacked the problem until Mr. Rose took it in hand. Although questions connected with assaying did not often come before the Society, they were matters to which the fathers of chemistry had given much attention. He might remind the Society that, apart from their scientific interest, these minute questions connected with assaying assumed considerable industrial importance. During his connection with the Mint, extending over more than twenty years, he had been responsible for the standard pureness of more than 600 tons of gold, the value of which was over 80 millions sterling. As regards the number of assays made, he and his two colleagues, the Assistant Assayers, had made in

the past year no fewer than 30,000 assays of gold, and they had every reason to believe that their average accuracy was 1-10,000th part.

*133. "Note on the Boiling-point of Nitrous Oxide at Atmospheric Pressure, and on the Melting-point of Solid Nitrous Oxide." By WILLIAM RAMSAY, F.R.S., and JOHN SHIELDS, Ph.D., B.Sc.

The boiling-point of the liquid nitrous oxide was found by means of a constant volume thermometer filled with hydrogen to be -89.8° ; and the melting-point of the solid to be -102.3° . The method adopted is one in which the errors due to the gas in the stem of the thermometer not being at the same temperature as that in the bulb and to the alteration of the capacity of the bulb by change of temperature are eliminated.

*134. "The Isomerism of the Paraffinic Aldoximes." By WYNDHAM R. DUNSTAN and T. S. DYMOND.

Several attempts have been made during recent years to obtain evidence of an isomerism in the series of paraffinic aldoximes similar to that which has been observed and studied in a number of the corresponding benzenoid derivatives. These attempts have so far been unsuccessful, and, in fact, it has been concluded from the recent experiments of Dollfus (*Ber.*, 1892, 1908) that paraffinic aldoximes exist only in one form. The fact that the paraffinic aldoximes were, until recently, known only in the liquid condition has, however, made such enquiries difficult if not inconclusive. The problem has assumed a new aspect since the authors' discovery that acetaldoxime could be crystallised, and that when heated for some time above their melting-point (m.p. 46.5°) the crystals gradually undergo isomeric change into a modification which is liquid at the ordinary temperature, but which, on cooling, slowly changes back again into the crystalline form. The physical differences between the two isomerides are for the most part very slight, there being but small differences in their relative densities and magnetic rotations. Further experiments have been made in order to compare these two modifications with the two isomeric benzaldoximes discovered by Beckmann, and, if possible, to determine the nature of the isomerism. Chemical experiments with the two modifications of acetaldoxime are difficult to carry out, owing to their instability and especially to the circumstance that the liquid modification cannot be obtained free from its someride.

When acted on by acetic anhydride neither modification furnishes any appreciable quantity of acetonitrile, except at temperatures near 100° . By working under conditions whereby the occurrence of isomeric change is minimised, the crystalline acetaldoxime is converted by acetic anhydride into a liquid acetyl derivative which is so unstable that it cannot be isolated in the pure state; it decomposes when distilled, even under reduced pressure. It is hydrolysed by water as well as by dilute alkalis, yielding acetic acid and the aldoxime. The liquid acetaldoxime also furnishes an acetyl derivative, which apparently is identical with that obtained from the crystalline isomeride. In some cases the action of acetic anhydride on both modifications has led to the production of a small quantity of *hydroxyacetylaldoxime* (*diacetyl-droxamic acid*), $\text{CH}_3\text{C}(\text{OH})\text{NO}(\text{COCH}_3)$, a solid crystalline substance melting at 87.5° .

Both modifications of acetaldoxime are converted by hydrogen chloride into the same crystalline hydrochloride ($\text{CH}_3\text{CH}:\text{N}\cdot\text{OH}\cdot\text{HCl}$), a very hygroscopic substance.

By the action of phosphoric chloride at a low temperature on an ethereal solution of the crystalline acetaldoxime a product is obtained which on hydrolysis gives ammonia and acetic acid as well as methylamine and formic acid. A determination of the quantity that is formed of each of these substances has shown that 90 per cent of the aldoxime is converted into ammonia and acetic acid, and the remainder into methylamine and formic acid. When acted on by phosphoric chloride at a

higher temperature, the liquid acetaldoxime is converted into a product which on hydrolysis furnishes the same products as the crystalline modification, and in almost the same proportion.

On the other hand, the two isomerides afford only ammonia and acetic acid when acted on by phosphorous chloride.

Propionaldoxime, $\text{C}_2\text{H}_5\cdot\text{CH}:\text{NOH}$, has hitherto been known only as a liquid (b. p. 132°); it may, however, be crystallised by cooling it to about -12° , and thoroughly stirring the liquid. The crystals closely resemble those of acetaldoxime in appearance; they melt at 22° , that is, 24.5° lower than the acetic compound. If it be melted and the resulting liquid be heated for some time, propionaldoxime gradually undergoes an isomeric change similar to that suffered by acetaldoxime, being converted into a liquid which cannot be made to crystallise by any means unless it be cooled below -10° , when crystals of the other modification separate, and by degrees entire re-conversion into this form takes place.

There is only a slight difference in the relative densities of the two modifications. Phosphoric chloride acts on a well-cooled ethereal solution of the crystalline propionaldoxime, and when the mixture is poured into water ammonia and propionic acid are produced as well as ethylamine and formic acid. About 94 per cent of the aldoxime is converted into ammonia and propionic acid, and about 6 per cent into ethylamine and formic acid.

When acted on by phosphorous chloride, however, it affords only ammonia and propionic acid.

Isobutyric aldoxime is a liquid (b. p. 139.5°) which does not crystallise even when cooled to -80° . When acted on by phosphoric chloride, about 60 per cent of the aldoxime is converted into ammonia and isobutyric acid, and about 40 per cent into isopropylamine and formic acid.

It would appear from these results that further study is requisite to establish criteria of stereochemical isomerism in the case of these oximes. It would seem that the action of phosphoric chloride in particular is attended with structural isomeric change, and that the production by Beckmann's method of two acids and two amines cannot be regarded as evidence of the existence in the compound of two stereochemical forms of the original oxime, as has been suggested by Hantzsch, in the case of certain ketoximes.

It has, therefore, been determined to submit the two isomeric benzaldoximes to a more minute examination than they have hitherto received; these aldoximes being selected, rather than any of the paraffinoid compounds, on account of their greater stability. Progress has already been made with this work.

135. "The Mineral Waters of Askern, in Yorkshire." By C. H. BOTHAMLEY.

Although the mineral waters of Askern have a well-established reputation in the treatment of chronic rheumatism and of skin diseases, no analyses of them have been made since those of Lankester and West in or about the year 1840.

There are at present four wells or springs in the peat common, on the edge of which the village of Askern stands, and to each of these is attached a pump room and a suite of baths. The author has examined samples of the waters collected at intervals extending over a period of nearly two years. They are surface or shallow spring waters, and are mainly solutions of calcium and magnesium carbonates and sulphates, containing a large quantity of dissolved peaty matter and a considerable amount of hydrogen sulphide; minute traces of iodine and lithium, but neither bromine or potassium, were detected. The approximate composition of the four waters, in grms. per litre, is given in the Table.

It is pointed out that the production of the sulphuretted hydrogen is probably due to the action of an organism, although hitherto the author has failed in isolating one.

	Mother Close Well.	Terrace Baths.	Charity Baths.	Manor Baths.
Calcium carbonate ..	0.8417	0.8232	0.6825	0.6698
„ silicate.. ..	0.0281	0.0262	0.0443	0.0449
„ sulphate ..	0.5222	0.4434	0.4938	0.5151
Magnesium sulphate..	0.3874	0.4288	0.7184	0.6834
Sodium chloride . .	0.0346	0.0989	0.1190	0.1205
„ sulphate . .	0.0426	0.0220	0.0659	0.0599
Total	1.8566	1.8425	2.1239	2.0936

Hydrogen sulphide .. 56.7 c.c. 49.5 c.c. 34.8 c.c. 37.3 c.c.

136. "Note on the Distribution of Acidic and Alkaline Radicles in a Solution containing Calcium, Magnesium, Carbonates, and Sulphates; and on the Composition of Mineral Waters." By C. H. BOTHAMLEY.

In examining the mineral waters of Askern, it was found that the precipitate formed when the "free" carbon dioxide was expelled was almost pure calcium carbonate, and contained the merest trace of magnesium, although this element was present in considerable quantity. Direct experiments show that an excess of well-washed precipitated magnesium carbonate completely precipitates calcium from a solution of calcium sulphate in the absence of "free" carbon dioxide, and that there is practically no reverse action when a solution of magnesium sulphate is placed in contact with a large excess of precipitated calcium carbonate. When solutions of calcium carbonate and magnesium sulphate are mixed together and the "free" carbon dioxide is expelled by the action of heat or by the passage of a current of hydrogen, the precipitate contains only a mere trace of magnesium. The same result is obtained when a solution of magnesium carbonate is mixed with a solution of calcium sulphate and the "free" carbon dioxide is expelled by a current of hydrogen.

The existing thermochemical data afford no explanation of these results.

The author concludes that if we put aside the question of ionic dissociation in solution, and represent mineral waters and similar solutions of calcium, magnesium, and the carbonic and sulphuric acid radicles as containing salts as such, the sulphuric radicle must be regarded as combining by preference with magnesium and not with calcium, as is generally supposed. In the case of the Askern waters this view is supported by their therapeutic action.

137. "A Magnesium Compound of Diphenyl." By W. R. HODGKINSON.

The energetic manner in which ammonia gas and some ammonium salts are decomposed by magnesium suggested that perhaps benzenoid amines, and especially anilids, might give metallic derivatives. Magnesium, however, is entirely without action on dry aniline, toluidine, and other similar alkaloids; and form. and acetanilid and even phthalanil are unaffected when passed over the metal heated to about 400°.

When phenylhydrazine is warmed with magnesium, either in the form of filings, ribbon, or wire, action begins at about 150°; using filings, if not carefully controlled, the action becomes almost explosive, the temperature attained being frequently sufficient to inflame the products. The products which volatilise during the process are aniline, benzene, ammonia, and nitrogen; a compound containing the metal being left in the retort.

The magnesium compound is a solid, nearly white substance; it does not volatilise, but on heating the contents of the retort in which the operation has been conducted to nearly a red heat, an oil distils over from which a small quantity of diphenyl may be isolated. On admitting air into the retort before it is quite cold, the substance turns brown, and in most instances inflames. Water has a similar effect on the hot substance.

Boiling benzene, and especially cymene, dissolve a metallic compound which is deposited partly on cooling

and partly on evaporating off the solvent in a vacuum as a brown amorphous powder; this takes fire on very gently heating it in air, magnesium oxide and much charcoal being left.

As yet the analysis of different preparations of this substance have not been very satisfactory. It certainly does not contain much, if any, nitrogen as an essential element, the highest percentage found being 1.4; this appears to be derived from some nitrogen compound formed by a secondary action and not from a magnesium phenylhydrazine or magnesium aniline.

The unmistakable production of diphenyl on heating the magnesium compound is suggestive of the presence of magnesium diphenyl as one of the products.

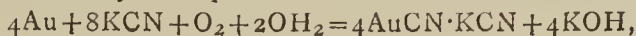
The author wishes to reserve the further investigation of the interaction.

138. "Note on Acetanhydrocitric Acid. By FELIX KLINGEMANN.

The author points out that the acetylanhydrocitric acid described by Easterfield and Sell (*Trans.*, 1892, 1003) had been previously prepared and studied by himself (*Berichte*, 1889, 983); he adversely criticises several of their statements, and quotes analyses of the silver salts of citrodianilic and citro-*p*-toluidic acids, proving that both are mon-acids.

139. "The Dissolution of Gold in a Solution of Potassium Cyanide." By R. C. MACLAURIN, B.Sc.

The study of the conditions contributory to the dissolution of gold in solutions of potassium cyanide is become of importance, owing to the recent use of this agent in extracting gold from poor ores. The nature of the changes is disputed; Elsner originally expressed the interaction by the equation—



but McArthur, in a recent paper, has called in question the necessity of oxygen being present. It is a remarkable fact in connection with the process that the rate of dissolution of the gold decreases as the concentration of the cyanide solution increases.

It is shown that dissolution of the metal is conditioned by oxygen, and that the amounts of oxygen absorbed and of gold dissolved are in the ratio O : 2Au. Furthermore, it is shown that the rate of dissolution varies with the strength of the solution, and that it passes through a maximum in passing from dilute to concentrated solution; this variation is traced to a decrease in solubility of oxygen in solutions of potassium cyanide as the concentration increases.

Annual General Meeting, March 27th, 1893.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

THE PRESIDENT delivered an address, of which the following is an abstract:—

The numerical position of the Society is as follows:—

Number of Fellows, March, 1892	1825
Since elected who have paid admission fees ..	128
	1953
Removed on account of non-payment of subscriptions	20
Withdrawn	18
Deceased	20
	58
Present number of Fellows	1895
Foreign Members (1892) .. .	30
Since elected.. . . .	5
Present number of Foreign Members .. .	35

Twenty Fellows have died within the year:—G. S. Bowler, H. N. Draper, John Hooker, A. W. von Hofmann,

F. C. Hills, W. E. Ivey, Hodgson Jones, Dr. G. D. Longstaff, W. H. Michael, G. H. Makins, J. S. Merry, Dr. T. H. Rowney, John S. Sieber, Professor C. Schorlemmer, A. Norman Tate, Thomas Taylor, Dr. Thos. Walton, J. Septibo Ward, Dr. J. Forbes Watson, Mattieu Williams.

Eighteen Fellows have withdrawn:—Thomas Akitt, Dr. James Bell, Edward Dillon, J. V. Elsdon, J. C. Husband, W. E. Halse, Farmer Hall, E. T. Kensington, Lawrence Levy, Chas. O'Neill, Dr. G. S. W. Ogg, Magnus Ohren, G. A. Parkinson, H. F. Pasley, Edward Purser, A. H. Tapp, E. W. Wiltshire, Dr. George Wilson.

The names of twenty Fellows have been removed from the Register:—James Anderson, Dr. J. B. Battershall, Frank Calder, G. E. R. Ellis, D. R. S. Galbraith, G. W. S. Howson, J. J. Hickey, A. C. M. Ingram, George Lloyd, H. Oliver Mintz, J. W. O'Connor, C. T. Rhodes, E. Reckett, W. Symons, H. L. Schubert, H. L. Sulman, Stanley Southam, T. B. Tyson, Dr. F. W. Traphagen, M. Whitley Williams.

Professors Emil Fischer, Carl Graebe, Adolph Liben, Hugo Schiff, and Th. Schloesing have been elected Foreign Members.

No fewer than 139 communications are recorded in the *Proceedings*, this being the largest number yet contributed to the Society in a single session.

The 1892 volume of the *Transactions* contains ninety papers, occupying 1096 pages, while the Abstracts occupy 1536 pages.

From the commencement of this year, the Abstracts have been so paged that it will be possible to bind them in two sections, the one section to include all papers on organic chemistry, the other the remaining branches; this arrangement has been adopted by the Council in the belief that it will tend to promote continuity and facilitate reference.

The Council have resolved that a subject index of the original communications published in the Society's Journal during the years 1873—1892 inclusive shall be published. It is suggested that this shall be a true index and not a mere recital of titles; the precise form it shall take is, therefore, under consideration.

Two "Memorial Lectures" have been delivered during the year, commemorating the work of two deceased Foreign Members, Hermann Kopp and Jean Servais Stas: that on Stas was prepared by Professor Mallet, and that on Kopp by the Treasurer, Professor Thorpe; the Society and chemists generally will undoubtedly feel that they are much indebted to both of these two gentlemen when the two memoirs are placed in their hands. In the first of these lectures, Professor Mallet, besides referring to Stas's work, has carefully considered its bearings and has indicated directions in which enquiries may, with advantage, be now carried on; the example that he has set will undoubtedly be of great service in the preparation of similar memoirs. The Council have resolved to print an extra number of copies of such lectures, and when in possession of a sufficient number to form a volume, to issue them in a separate form.

Among the Fellows deceased during the year there are two whose services to the Society have been of an altogether special character—Professor von Hofmann and Dr. G. B. Longstaff; special resolutions of condolence have been passed by the Council and communicated to their families. Von Hofmann's work will be considered in the coming Hofmann Memorial Lecture. In Dr. Longstaff the Society loses one of its original Fellows, of whom now very few remain. He was a very active member of the Society in early days, and within recent years his munificence secured the establishment of the Research Fund; owing to his stipulation that a medal should be awarded at least triennially to a Fellow of the Society in recognition of the value of his researches, Dr. Longstaff's name will ever remain associated with the Society and with chemical science, as the Council determined that the medal should be known as the Longstaff Medal.

Towards the close of the year, an address, offering the Society's congratulations on the occasion of the celebration of its twenty-fifth anniversary, was forwarded to the *Ber. Deuts. Chem. Gesell.*

An address from the Society was presented to M. Pasteur on the occasion of his 70th birthday.

Communications were addressed by the Foreign Secretary to the University of Padua on the occasion of the Galileo celebration, and to the Committee in Stockholm, charged with the erection of a memorial to Scheele in response to invitations to the Society to take part in these proceedings.

The Council are indebted to Mr. E. H. Wollaston for the presentation of a valuable proof engraving of a portrait of Wollaston.

Very considerable additions have been made to the library during the year.

The subject of the admission of women as Fellows, which has been several times discussed by the Council, has been again brought under consideration during the year, but without any resolution being arrived at to propose an alteration in the Bye-laws. It appeared to be generally felt that, although there is no objection in principle to the admission of women as Fellows, the case in their favour is not clearly established by any considerable number of applications.

During the long vacation the meeting room was entirely reconstructed, with the result that a very considerable air space has been gained, tending to the better ventilation of the room; additional accommodation both in sitting space and in entrances and exits has also been secured; and provision has been made for the entrance of fresh air into, and for the removal of vitiated air from, the room. The electric light has been substituted for gas in all the rooms. The apartments were redecorated throughout.

The structural alterations were planned and their execution superintended by Mr. Martin L. Saunders, and the alterations and redecoration of the rooms have been carried out by Messrs. Colls and Sons. The installation of the electric lighting was planned by Prof. Ayrton, to whom the Society is under great obligation for the amount of time and thought he has expended on the work. The business of wiring the building and fixing the fittings for the electric light was entrusted to Messrs. Spagnoletti and Crookes, and the brackets, pendants, &c., were supplied by Messrs. Faraday and Sons.

	£	s.	d.
The cost of the structural alterations (including architect's fee) have been ..	1113	14	10
The electric light installation having cost	289	0	6

£1402 15 4

It is a matter of congratulation to the Society that the Treasurer has been able to pay these large extra expenses, and at the same time to carry forward the necessary working balance, without touching the Society's funded property.

In the latter part of his address the President discusses the history of the phlogistic theory, and its gradual displacement by more modern views.

Dr. ARMSTRONG proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed. In the course of his remarks, he said that during the past two years, for the first time in the history of the Society, the President had been a Fellow from beyond the Border,—a fact of much importance, as proving that they were in no sense a mere metropolitan society, and that they both desired to secure, and were, indeed, successful in securing, the cooperation of British chemists generally. Dr. GLADSTONE seconded the motion, which was carried by acclamation. The PRESIDENT having thanked the meeting,

Mr. HOLLAND CROMPTON, the Senior Auditor, in the absence of the Treasurer abroad, gave an account of the balance sheet duly audited by Mr. Dymond, Dr. Lawson,

and himself. Prof. Thomson subsequently contrasted the chief items of expenditure during this and the previous year. The receipts by admission fees and subscriptions had been £3771 11s. 4d. as against £3545 in the previous year; and £424 15s. 3d. had been realised by the sale of the Journal, instead of only £408 7s. 4d. The Journal had cost £2745 7s. 4d. instead of £2798 15s. 10d.; £327 1s. 1d. had been expended on the library; the alterations had been effected at a cost of £1402 15s. 4d.; the total expenditure being £5287 1s.; so that the ordinary expenditure had been £3884 5s. 8d. as against £3989 1s. 6d. in the previous year. Grants amounting to £200 had been made from the Research Fund.

A vote of thanks to the Treasurer was proposed by Dr. RUSSELL, who dwelt with satisfaction on the fact that it had been possible to meet the expenses of the alterations from the surplus income of this and the previous year without touching the Society's funded property. The vote, having been seconded by Prof. RAMSAY, was carried by acclamation.

Mr. CROOKES proposed and Mr. PICKERING seconded a vote of thanks to the Auditors; the motion having been adopted, Mr. CROMPTON replied.

A vote of thanks to the Officers and Council was then proposed by Mr. J. NEWLANDS and seconded by Mr. CASSAL; Prof. THOMSON replied.

Dr. J. VOELCKER moved and Mr. SPILLER seconded a vote of thanks to the Editor, Sub-Editor, Abstractors, and Librarian. Mr GROVES and Dr. THORNE replied.

Mr. W. Foster and Mr. Tutton having been appointed Scrutators, a ballot was taken, and the following were declared elected:—

President—H. E. Armstrong, Ph.D., F.R.S.

Vice-Presidents who have filled the office of President—

Sir F. A. Abel, K.C.B., D.C.L., F.R.S.; Dr. A. Crum-Brown, F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Lord Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—E. Atkinson, Ph.D.; A. Vernon Harcourt, F.R.S.; C. O'Sullivan, F.R.S.; John Pattinson; William Ramsay, F.R.S.; William A. Tilden, F.R.S.

Secretaries—J. Millar Thomson; Wyndham Dunstan, M.A.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—T. E. Thorpe, D.Sc., F.R.S.

Ordinary Members of Council—Norman Collie, Ph.D.; Charles F. Cross; Harold Dixon, F.R.S.; Bernard Dyer, D.Sc.; Lazarus Fletcher, M.A., F.R.S.; R. J. Friswell; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; W. A. Shenstone; John A. Voelcker, Ph.D.; W. P. Wynne, D.Sc.

The following additions to the bye-laws, proposed by the Council, were then submitted to the meeting and carried:—

1. In Bye-Law XI., after the words: "The ordinary Scientific Meetings of the Society shall be held twice in every month, from November to June inclusive, except in the month of January, when the Society shall meet once only," to add the words "and also at Easter, when, if the Council see fit, there shall also be only one meeting in the month."

2. In Bye-Law XIII. to add the following paragraph:—
"At all General Meetings of the Society, whether Annual or Extraordinary, no motion of a proposal to alter the bye-laws shall be considered of which due notice has not been given at least 14 days previously, either at an ordinary Scientific Meeting, or through the agency of the *Proceedings*, or by means of a printed notice addressed to all the resident Fellows."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 13, March 27, 1893.

Organic Matters Constituting Vegetable-Soil.—MM. Berthelot and André.—The author gives analyses of different soils of the Agricultural Station of Meudon. Close I. contains—

Organic carbon	19.1
Hydrogen	1.5
Nitrogen	1.7
Organic oxygen	11.9

Total organic matter .. 34.2

The authors remark that this is the only soil in which the complete determination of all the elements, mineral and organic, has been effected. This soil is said to be nearly saturated with nitrogen, whilst the soil II., equally rich in carbon, remains capable of absorbing free nitrogen. The authors recognise the action of microbia as gradually transforming barren sands into vegetable mould.

Researches on Samarium.—Lecoq de Boisbaudran.—This paper will be inserted in full.

Distillation of Mixtures of Water and Alcohol.—E. Sorel.—This paper does not admit of useful abstraction.

General Method for Calculating the Atomic Weights according to Chemical Analysis.—G. Hinrichs.—The author considers that the researches of an entire century have established the fact that if we take $O = 16$, the atomic weights of almost all the elements border very closely upon whole numbers; for others, such as Cu and Cl, the value is close upon a whole number and a half. "We may affirm that the most precise determinations of the elements are exactly what they ought to be if all the elements had been formed from a single primitive substance."

Formation of Gallanilide: its Triacetic and Tribenzoylic Derivatives.—P. Cazeneuve.—Aniline gallate, if heated to from 105° — 110° loses CO_2 , is transformed into gallanilide by the elimination of water. The anilide of gallic acid may be obtained by causing aniline to react upon digallic acid or gallotannic acid.

No. 14.

Benzenazocyanacetic Ethers and their Analogues.—A. Haller and E. Brancovici.—The authors have studied in detail the ethyl- and methyl-benzenazocyanacetates, their constitution, accepting them as true azo-derivatives and not as hydrazone. They also interpret the nature of the isomerism of the α - and β -ethers.

Attempt at the Condensation of the Acetyl-cyanacetic Ethers with the Phenols.—A. Held.—It results that the ethylacetylcyanoacetate behaves in a different manner according to the nature of the phenol employed. In the case of normal phenol it yields a substitution and transformation-product of malonic ether, the phenol not entering into reaction. In case of resorcin the nitrile function is saponified, and the same product is obtained as by the condensation of acetyl-acetic ether with resorcin. With methyl-acetylcyanoacetate, no appreciable transformations are produced. If dehydrating agents are employed other than sulphuric acid, such as zinc or aluminium chlorides, the result is nil.

Synthesis of Erythrite.—G. Griner.—The author has set out from a non-saturated carbide, divinyl or butadiene, and has obtained an (optically) inactive erythrite incapable of being split up. He is now attempting the formation of a racemic erythrite.

Action of Temperature on the Rotatory Power of Liquids.—A. Aignan.—If we calculate the effect on the polarimeter produced on a given radiation by a mixture of two active substances of opposite signs, we see easily that this effect may be nil for suitable proportions of the weights of the two bodies mixed. If there be given such a mixture which is thus *inactive by compensation*, its effect is examined at the same temperature upon a radiation different from the former, it is generally found inactive in one or other direction. If the effect produced by this liquid on the original radiation is examined at different temperatures, we may find that the compensation ceases to exist.

MISCELLANEOUS.

Technical Education at Cambridge.—The Cambridge University extension authorities have already announced as part of the programme of their summer meeting, to be held in Cambridge next Autumn, five courses of practical work in science in the University laboratories and museums, the subjects selected being chemistry, electricity, botany, physiology, and geology. As, however, the date of the summer meeting, July 29 to August 26, is too early for many teachers in elementary schools, whose holidays fall during harvest time, arrangements have also been made for two courses in agricultural chemistry, specially adapted to meet the requirements of teachers sent with scholarships by their respective County Councils. Each course will extend from August 25 to September 12 inclusive, and will thus include sixteen working days, on each of which several hours' work in the University laboratory will be provided. One course—conducted by Mr. Fenton, one of the University demonstrators—is intended for students who have done little or no laboratory work, but have acquired a knowledge of theoretical chemistry, and will be similar to the course given last year, and attended by about 120 County Council scholars. The other course—conducted by Mr. R. H. Adie, one of the Cambridge extension lecturers—will be more advanced in character, and will be adapted to students who went through last year's course with credit, or have done similar work elsewhere. Accommodation for 120 students can be provided at these two courses.

MEETINGS FOR THE WEEK.

- MONDAY, 24th.—Medical, 8.30.
— Society of Arts, 8. "Some Masters of Ornament," by Lewis Foreman Day. (Cantor Lectures).
TUESDAY, 25th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
— Royal Institution, 3. "Symbolism in Ceremonies, Customs, and Art," by John Macdonell, LL.D.
WEDNESDAY, 26th.—Geological, 8.
— British Astronomical Association, 5.
— Society of Arts, 8. "The Optical Correction of Photographic Perspective," by H. Van der Weyde.
THURSDAY, 27th.—Royal, 4.30.
— Royal Institution, 3. "The Atmosphere," by Prof. Dewar, F.R.S.
— Society of Arts, 4.30. "Indian Manufactures—their Present State and Prospects," by Sir Juland Danvers.
— Institute of Electrical Engineers, 8.
FRIDAY, 28th.—Royal Institution, 9. "The Transmission of a Nervous Impulse," by Prof. Francis Gotch, F.R.S.
— Physical, 5. "Discussion on the Viscosity of Liquids," by Prof. J. Perry, J. Graham, and L. W. Heath. "On Luminous Discharges in Electrodeless Vacuum Tubes," by E. C. Rimington.
SATURDAY, 29th.—Royal Institution, 3. "Some Applications of Electricity to Chemistry," by James Swinburne, M.Inst.E.E. (The Tyndall Lectures).

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THE CHEMICAL NEWS.

VOL. LXVII, No. 1744.

THE PRESENCE AND ESTIMATION OF GOLD AND SILVER IN ANTIMONY AND IN BISMUTH.*

By ERNEST A. SMITH, Assoc. R.S.M.,
Assistant Instructor in Assaying, Royal School of Mines, London.

GOLD and silver are found associated in larger or smaller quantities with most of the ores of antimony and of bismuth. It is therefore interesting to ascertain to what extent, with the modern methods of extraction, these metals are retained in the metallic antimony and bismuth as they come into the market. The usual methods for estimating the gold and silver present in antimony are scorification and methods involving solution, but in the former case, as not less than 500 grains of antimony have to be operated upon, the method cannot be recommended on account of the large quantity of lead necessary to ensure the elimination of the whole of the antimony. Wet methods also are scarcely applicable, owing to the very small percentage of precious metals contained in the mass of metallic antimony operated upon.

The following method was used and gave very satisfactory results:—

500 grains of the sample of metallic antimony crushed to a fine powder were mixed with—

Litharge	1000 grains.
Potassium nitrate	200 „
Sodium carbonate	200 „

and heated in a crucible in a wind furnace at a dull red heat for about fifteen minutes.

When quite tranquil the contents were poured into an ingot mould, and the button of lead, which weighed about 500 grains and was perfectly malleable, was cupelled direct. The resulting gold and silver button was parted in dilute nitric acid in the usual way.

When necessary the slags were cleaned by crushing to a coarse powder, mixing with 500 grains of litharge and 20 grains of charcoal, and fusing under the same conditions as before.

The following results were obtained with various samples of commercial star antimony:—

No. of sample.	Per ton of 2240 lbs.					
	Gold.			Silver.		
	Ozs.	Dwt.	Grs.	Ozs.	Dwt.	Grs.
1	0	19	14	1	15	7
2	1	12	0	0	5	5
3	0	4	14	6	4	19
4	0	1	7	0	17	0
5		trace		0	9	19
6	0	0	16	0	15	0
7	1	15	7	1	12	16
8	0	13	17	0	8	12

To estimate the gold and silver in metallic bismuth 500 grains were carefully cupelled, and the buttons of precious metals thus obtained were parted in the usual manner.

The results obtained for bismuth from various sources, recently purchased in London, are as follows:—

No. o Sample.	Per ton of 2240 lbs.					
	Gold.			Silver.		
	Ozs.	Dwt.	Grs.	Ozs.	Dwt.	Grs.
1	0	11	18	72	16	22
2 Australian.	3	11	21	108	8	10
3 German.	0	1	23	23	16	21
4 American.	0	3	6.5	23	0	14

The bismuth may be extracted from the cupels by rejecting the white portion and crushing the stained portion to a fine powder and fusing at a red heat with the following fluxes:—

Powdered cupels.. .. .	1000 grains.
Fluorspar	800 „
Soda carbonate	400 „
Borax	200 „
Charcoal powder.. .. .	45—50 „

From the results of the quantities of gold and silver obtained from the various samples of metallic antimony and bismuth it is somewhat remarkable that more profitable methods have not been introduced for the extraction of the precious metals.

THE COMBINATION OF OXYGEN WITH HYDROGEN.

By H. N. WARREN, Research Analyst.

A MIXTURE of two volumes of hydrogen with one of oxygen remains inert until a light is presented to the same,—so read our modern handbooks of chemistry. But oxygen, in admixture with hydrogen, becomes closer allied to water on increase of pressure, until a pressure of 180 atmospheres is attained, when combination takes place with fearful violence. The experiments which are thus presented by the author, of which a brief description will suffice, were constructed electrolytically, as may be readily observed to be the simplest and at the same time most efficient mode of dealing with the gases. Small selected glass tubes, into which two platinum wires were sealed, after introducing into each a c.c. of acidulated water and sealing the further extremity, were subjected to the action of an electric current of six volts. The rapid bursting of the first series of tubes, consequent upon the heating of the small quantity of liquid contained therein, at once suggested the cooling of the same by inserting the sealed tube and its contents in a strong glass vessel containing water. A tube thus mounted was next put upon trial; the electric circuit having been established, the experimenters meanwhile withdrawing themselves to a safe distance, carefully timing the effect.

In previous cases of trial the tubes had burst within three minutes, after applying the current, with a slight explosion; but in this case ten minutes had elapsed, and the action continued as energetic as ever. Fifteen and twenty minutes passed, and the action within the minute vessel continued as briskly as ever; exactly twenty-five minutes had elapsed when a vivid flash, succeeded by a violent report, terminated the experiment, shattering the glass vessel and scattering fragments in all directions.

Some force of the explosion may be understood from the fact of the sealed tube being but an inch and a half in length, and containing only one c.c. of water; nevertheless, portions of glass were hurled with sufficient force in the immediate neighbourhood of the explosion so as to penetrate a wooden bench to the depth of half an inch, whilst an assistant some distance from the spot narrowly escaped severe laceration. Various other tubes were afterwards experimented upon, affording similar results, the pressure, as arrived at by a careful average, amounting to 180 atmospheres.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

* Abstract of a Paper read before the Society of Chemical Industry, Monday, April 10.

DETECTION OF EXTRACTED TEA.

By W. A. TICHOMIROW.

THE author has made an examination of such tea as is used for the falsification of genuine tea. If dry extracted tea is covered with a cold, saturated solution of copper acetate, the blue colour of the liquid remains unchanged for months. With dry fresh tea (not extracted), the original blue colour of the liquid is found on the second day to have been changed into a greenish blue, and subsequently to a pure green. The leaflets of the fresh (not extracted tea), remain strongly contracted and rolled up even after steeping in the water for weeks, whilst tea which has been previously extracted unrolls perfectly without any previous immersion in water.

The characteristic distinction between extracted and fresh tea is shown by the idioblasts. If microscopic sections of leaves which have been steeped for from 1 to 4 days in a cold saturated solution of copper acetate are touched with a drop of the "liquor ferri acetici" of the Russian Pharmacopœia (specific gravity 1.134 to 1.138), and examined under the microscope, all the histological elements which contain tannin have taken a deep, black-blue colour. The tannins are fixed in their normal places by the previous treatment with copper acetate.

In leaves which have been previously extracted, the cell-walls have been previously permeated by the tannin dissolved in water, whilst in fresh tea they remain colourless, because the tannins are found normally not in the idioblasts, but in the surrounding parenchyma-cells. The shrivelling and the inability to unroll in water the tea-leaves which have not been previously extracted with hot water must depend on the formation of a dense, solid, copper tannate, insoluble in water. It is a kind of tannin which prevents the turgescence of the tissues.

E. Hanausek (*Zeit. f. Nahrungsmittel Untersuchung*) detected the appearance of a green colour also in extracted tea, and in his experiments the idioblasts did not show sharply and consistently the expected microchemical reactions, probably in consequence of the complete exhaustion of the leaves. Hanausek's further experiments had the purpose of determining the refractive index of the infusion of tea as a distinction between extracted and recent tea.

As these experiments are not completed, and as the determination of the proportion of extract afford a more certain basis than the indices of refraction which do not differ very widely among themselves, we must refer to the original.—*Pharm. Zeit. Russland's*.

THE MICROCHEMICAL RECOGNITION OF SULPHUR.

NOTICE ON THE USE OF GASEOUS REAGENTS, ESPECIALLY THE VAPOUR OF BROMINE, IN MICROCHEMICAL ANALYSIS.

By F. EMICH.

THE author's purpose is to show that in many cases gaseous reagents may be advantageously used in microchemical analysis. Bromine vapour seems capable of various applications as a convenient and energetic oxidising agent. It is recommended if sulphur, whether free or as a metallic sulphide, is to be shown in the form of gypsum.

The substance to be tested is moistened with solution of calcium chloride (concentration from 5 to 25 per cent), and exposed to vapours of bromine, the port-object, with the drop downward, being laid over a bottle containing saturated bromine water. The sulphur (of course with a preliminary formation of bromine sulphide) is converted into sulphuric acid, which produces with the calcium chloride the characteristic needles of gypsum.

With free sulphur, or finely-divided sulphides, as obtained by precipitation, the oxidation is so rapid that an exposure to the fumes of bromine for three to five minutes suffices for producing abundant formation of gypsum. Natural or fused sulphides are attacked more slowly, but after trying more than fifty I have met with none which did not yield calcium sulphate on sufficiently prolonged exposure to the vapour of bromine. Hence, without doubt, the reaction may be characterised as universally applicable. In many cases it may prove superior to fusion with soda and saltpetre, which has been recommended in the *Zeit. Anal. Chemie*, xxx., 166.

As in this process we add no more liquid to the original drop, the gypsum crystallises rapidly. With a slight dust of "milk of sulphur" the reaction succeeds perfectly, except too much solution of calcium chloride has been taken. I have dissolved 0.5 grm. pure sulphur in 50 c.c. of pure carbon disulphide. The residue of one m.grm. of the solution, i.e., 0.001 m.grm. sulphur, gave the reaction readily. If the above sulphur solution was diluted to the 50th, one m.grm. of the new solution evaporated down on the port-object, the scarcely perceptible speck of sulphur (0.00003 m.grm.), touched with the solution of calcium chloride by means of a platinum needle, and then exposed to bromine, numerous tufts of crystals of gypsum were detected with a magnifying power of 300 diameters. Hence, the 50,000th part of a m.grm. of sulphur can be certainly recognised by this test.

If a grain of mustard-seed is steeped over night in a solution of calcium chloride, and then exposed for some hours to the fumes of bromine, it is found covered with crystals of gypsum.

In order to convert an arsenical mirror into magnesium ammonium arseniate, it is formed on a port-object, treated with moist vapour of bromine, and then after the addition of a trace of solution of magnesium sulphate, again fumed with dilute ammonia.

If we mix a solution of potassium iodide with a few granules of starch, and treat it with the vapour of red nitric acid, it is easy to obtain the blue colour with 0.0001 m.grm. KI (containing 0.00007 m.grm. I).—*Zeit. Anal. Chemie*, xxxii., p. 163.

DETERMINATION OF THE SALTS OF IRON BY AN IODOMETRIC METHOD.

APPLICATION OF THE METHOD TO THE DETERMINATION OF IRON IN ORES.

By EDOUARD NIHOUL.

It is known that ferric salts react with potassium iodide in presence of an acid. Under ordinary conditions the reaction is not completed, there remaining potassium iodide undecomposed and ferric salt not reduced to the ferrous state.

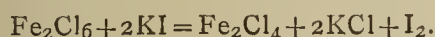
M. Duflos proposed to render this transformation quantitative by heating under pressure the mixture of ferric salt, potassium iodide, and hydrochloric acid; the free iodine is then determined in presence of ferrous salts by sodium thiosulphite. But this procedure is not merely scarcely practicable, but it often gives discordant results. We think it more convenient to eliminate the iodine by distillation as it is formed, and to determine it in the absence of ferrous salts. In our first attempts we nevertheless operated in presence of these salts. The operation is effected by means of an arrangement analogous to that which we made use of for the determination of nitrates and chlorates.

The apparatus consists of a flask for fractionated distillation, closed with a tubulated stopper in which is passed a tube bifurcated at its upper end. One of the branches of the tube is in communication with an appa-

ratus for carbonic acid, whilst the other serves for the introduction of the potassium iodide. This latter may be ultimately put in communication either with a steam-pipe or an apparatus for gaseous hydrochloric acid. The products of distillation are received in a Volhard's condenser, containing a solution of potassium iodide.

The ferric salt is introduced either as a solid or in solution into the apparatus for fractionated distillation, hydrochloric acid is added, and it is dissolved by the aid of heat if needful. The apparatus is cleared from the air which it contains by means of a current of carbonic anhydride. When all the air is expelled, we introduce a small excess of a rather concentrated solution of potassium iodide by means of a small pipette, the tube of which is placed in communication with the free branch of the bifurcated tube. The contents of the flask are heated to ebullition, still keeping up a slight current of carbonic anhydride.

After ten to fifteen minutes the iodine has passed almost in totality into the Volhard flask, where it is condensed. The contents of the flask are added to the distillate, and the iodine is determined in the total liquid by a solution of sodium thiosulphite, normal or decinormal, according as we operate on a smaller or larger quantity of iron. The ferric salts react with potassium iodide according to the following formula—



0.4416 of iron corresponds to 1 part of iodine.

Care must be taken in the application of this method to allow the contents of the flask to cool, on distillation, with exclusion of air, in a current of carbonic anhydride. The determination should be made very rapidly so as to prevent the possible return of a part of the ferrous salts to the ferric state. 50 c.c. of a ferric solution containing 4 grms. iron per litre gave 0.1996 of iron in place of 0.200; 10 c.c. of the same solution gave 0.0401 in place of 0.0400.

In order to verify the accuracy of this process, we executed under the same conditions a new qualitative operation, which showed the absence of ferric salts in the flask after distillation of two-thirds of the original solution. We may avoid adding the contents of the flask to that of the condenser for the determination of the iodine. For this purpose it is sufficient to eliminate the iodine completely by distillation. This may be effected by several procedures.

(I.) We add concentrated hydrochloric acid in several portions during the operation, especially at the end. Under these conditions the excess of potassium iodide is decomposed and transformed into chloride, the iodine is no longer retained in the apparatus, and distils with the hydriodic acid formed during the reaction.

A practical trial under these conditions on the distillate alone gave 0.0395 grm. in place of 0.0400 grm. of iron employed. Instead of using hydrochloric acid in a concentrated solution, it is advantageous to make use of gaseous hydrochloric acid if we have a suitable apparatus at hand.

(II.) We may employ a current of steam. However, the distillation of iodine is slow and is not complete as long as there remains undecomposed potassium iodide, in consequence of the energy with which this salt retains iodine. It has no real advantage except in cases where the excess of potassium iodide has been previously destroyed. In the use of the method the following precautions should be taken:—

1. Refrigerate the Volhard condenser so as to condense the vapours of iodine rapidly.

2. Make use, as far as possible, of stoppers which have been used two or three times; the action of iodine vapours on a new stopper constitutes an appreciable loss when operating upon small quantities.

3. Place after the Volhard flask a second similar condenser in cases where we operate upon large quantities of ferric salts.

Determination in Ores.

The Iron is Present in the Ferric State.—We weigh from 0.3—0.5 grm. of the ore finely powdered, and introduce it into the flask for fractionated distillation. We add 25 c.c. of concentrated hydrochloric acid, and then introduce a slow current of gaseous hydrochloric acid, heating meanwhile almost to ebullition. In this manner the hydrochloric acid is always kept at its maximum of concentration, and the solution is made very rapidly. The apparatus is then put in connection with Volhard's condenser. A current of carbonic anhydride is then introduced. Then we pour into the flask the solution of potassium iodide in slight excess, and heat to ebullition. When the chief part of the iodine has been distilled, small quantities of gaseous hydrochloric acid are repeatedly introduced to the residue; and when all the iodine has disappeared it is determined in the distillate by means of solution of thiosulphate. It is sometimes advantageous to introduce into the flask before the action a small crystal of potassium iodide, the hydriodic acid considerably facilitating the solution of the ore. We may even introduce at the outset all the potassium iodide necessary for the reaction. In these two latter cases care must be taken to sweep out the apparatus with carbonic anhydride in order to avoid the action of oxygen upon the hydriodic acid set at liberty.

The assay of an ore performed with and without the previous addition of potassium iodide, has given us successively, 51.4 and 51.9 per cent. The analysis by the permanganate process gave 51.7 per cent.

The Iron is in the Ferrous State, or simultaneously in the Ferrous and Ferric States.—We dissolve, as above, with gaseous hydrochloric acid, but without the previous addition of potassium iodide. When the solution is completed, we add some crystals of potassium chlorate or permanganate, and we continue whilst maintaining the liquid at ebullition to introduce a current of hydrochloric acid until the chlorine has entirely disappeared. The apparatus is then swept out with carbonic anhydride, the flask is re-connected to the condenser, the potassium iodide is introduced, and the operation is completed as in the former case.

Supplementary Note on the Iodometric Determination of Iron in Ores.

The only difficulty presented by the process above described lies in the complete expulsion of the iodine from the flask for fractionated distillation, in which the reaction is effected between the ferric salt and the potassium iodide. We have indicated the two following methods as enabling us to reach this result.

1. Destroy the excess of potassium iodide by hydrochloric acid, as the potassium iodide obstinately retains the last portions of iodine.

2. Introduce a current of steam into the apparatus at the end of the operation. Under the conditions of the experiment this latter process offers no real advantage.

At the advice of Prof. de Koninck we have substituted hydriodic acid in solution for potassium iodide. Under such conditions the iodine is no longer retained so obstinately in the flask, and it may be easily expelled at the end of a few minutes by a current of steam. The following experiments demonstrate this. They have been made with quantities of a solution of known strength accurately measured.

Iron taken.	Iron found.
0.0278	0.0276
0.0557	0.0557
0.0835	0.0834

We have further satisfied ourselves that the contents of the flask, after distillation, no longer contained a trace of free iodine. In the application of the method to the analysis of ores, the use of hydriodic acid presents also the advantage of avoiding the use of gaseous hydrochloric

acid. In fact, the solution of the ore may be very well effected by a mixture of concentrated hydrochloric and hydriodic acid. This method can evidently be used only if the iron in the substance to be analysed is entirely in the ferric state.

Commercial hydriodic acid often contains small quantities of free iodine. Its proportion of iodine must therefore be determined at the moment of the operation so as to be taken into account in the final result; or this iodine may be made to disappear by the addition of stannous chloride in the proportion exactly necessary.

The commercial product, obtained by means of phosphorus, sometimes gives off a faint odour of phosphamine, but we have found that this has no influence on the accuracy of the results.—*Revue Universelle des Mines et de la Metallurgie*, xxi., No. 1.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1893.

By WILLIAM CROOKES, F.R.S.,

and

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, April 14th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

In our previous report for the month of February we called attention to the degree of colour-tint of the water then being supplied, which, though insufficient to be noticeable in small bulks of the water, became very apparent on its being submitted to definite colorimetric examination. During the first ten days or so of the succeeding month of March, while the river still continued in flood, the degree of colour-tint of the supply, taken notice of in our previous report, did not manifest any appreciable reduction; but during the remainder of the month, alike in degree of freedom from colour-tint and in the smallness of the amount of organic matter present, the condition of the water supply was unexceptional.

In the supply for the entire month, indeed, taking the Thames-derived water for illustration, the mean proportion of organic carbon present was found to be 0.172 part in 100,000 parts of the water, with a maximum of 0.272 part in any single sample examined—as against a mean of 0.185 and maximum of 0.286 part in the previous three months' supply. Again the mean amount of oxygen required to oxidise the organic matter present was 0.057 grain per gallon of water, as against a mean of 0.063 grain per gallon in the previous three months' supply.

Of the entire 182 samples of water examined during the month, three were recorded as wanting in brightness, and

one as being slightly turbid, the remaining 178 samples being well filtered, clear, and bright.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

ON THE DENSITIES OF THE PRINCIPAL GASES.*

By Lord RAYLEIGH, Sec. R.S.

(Continued from p. 185).

The Weights.

THE object of the investigation being to ascertain the ratio of densities of water and of certain gases under given conditions, the absolute values of the weights employed is evidently a matter of indifference. This is a point which I think it desirable to emphasise, because v. Jolly, in his, in many respects, excellent work upon this subject (*Munich Acad. Trans.*, vol. xiii., II., 49, 1880), attributes a discrepancy between his final result for oxygen and that of Regnault to a possible variation in the standard of weight. On the same ground we may omit to allow for the buoyancy of the weights as used in air, since only the variations of buoyancy, due, for example, to changing barometer, could enter; and these affect the result so little that they may safely be neglected.†

But, while the absolute values of the weights are of no consequence, their relative values must be known with great precision. The investigation of these over the large range required (from a kilogram. to a centigram.) is a laborious matter, but it presents nothing special for remark. The weights quoted in this paper are, in all cases, corrected, so as to give the results as they would have been obtained from a perfectly adjusted system.

The Water Contents of the Globe.

The globe being packed in finely-divided ice, was filled with boiled distilled water up to the level of the top of the channel through the plug of the tap, that is, being itself at 0°, was filled with water also at 0°. Thus charged the globe had now to be weighed; but this was a matter of some difficulty, owing to the very small capacity available above the tap. At about 9° there would be a risk of overflow. Of course the water could be retained by the addition of extra tubing, but this was a complication it was desired to avoid. In February, 1892, during a frost, an opportunity was found to effect the weighing in a cold cellar at a temperature ranging from 4° to 7°. The weights required (on the same side of the balance as the globe and its supports) amounted to 0.1822 grm. On the other side were other weights whose values did not require to be known so long as they remained unmoved during the whole series of operations. Barometer (corrected) 758.9 m.m.; temperature 6.3°.

A few days later the globe was discharged, dried, and replaced in the balance with tap open. 1834.1701 grms. had now to be associated with it in order to obtain equilibrium. The difference,—

$$1834.170 - 0.182 = 1833.988,$$

represents the weight of the water less that of the air displaced by it. The difference of atmospheric conditions was sufficiently small to allow the neglect of the variation in the buoyancy of the glass globe and of the brass counterpoises.

* A Paper read before the Royal Society.

† In v. Jolly's calculations the buoyancy of the weights seems to be allowed for in dealing with the water, and neglected in dealing with the gases. If this be so, the result would be effected with a slight error, which, however, far exceeds any that could arise from neglecting buoyancy altogether.

It remains to estimate the actual weight of the air displaced by the water under the above mentioned atmospheric conditions. It appears that, on this account, we are to add 2.314, thus obtaining—

1836.30

as the weight of the water at 0° which fills the globe at 0°.

A further small correction is required to take account of the fact that the usual standard density is that of water at 4° and not at 0°. According to Broch (Everett's "C.G.S. System of Units"), the factor required is 0.99988, so that we have—

$$\frac{1836.30}{0.99988} = 1836.52$$

as the weight of water at 4° which would fill the globe at 0°.

Air.

Air drawn from outside (in the country) was passed through a solution of potash. On leaving the regulating tap it traversed tubes filled with fragments of potash, and a long length of phosphoric anhydride, followed by a filter of glass wool. The arrangements beyond the regulating tap were the same for all the gases experimented upon. At the close of the filling it was necessary to use a condensing syringe in order to force the pressure up to the required point, but the air thus introduced would not reach the globe. It may be well to give the results for air in some detail, so as to enable the reader to form a judgment as to the degree of accuracy attained in the manipulations.

Date.	Globe empty.	Globe full.	Temp. of manometer.	Correction to 15°.	Corrected to 15°.
1892.					
Sept. 24	2.90941				
" 27	—	0.53327	17.8	-0.00112	0.53219
" 28	2.90867	—			
" 29	—	0.53271	15.7	-0.00028	0.53243
Oct. 1	2.90923	—			
" 3	—	0.53151	12.7	+0.00093	0.53244
" 4	2.90872				
		Tap re-greased.			
" 7	2.91036				
" 8	—	0.53296	12.4	+0.00105	0.53401
" 10	2.91056				
" 11	—	0.53251	11.8	+0.00129	0.53380
" 12	2.91039				
" 13	—	0.53201	11.0	+0.00161	0.53362
" 14	2.91043				
" 15	—	0.53219	10.6	+0.00177	0.53396

The column headed "globe empty" gives the (corrected) weights, on the side of the working globe, required for balance. The third column gives the corresponding weights when the globe was full of air, having been charged at 0° and up to the pressure required to bring the mercury in the manometer into contact with the two points of the measuring rod.

This pressure was not quite the same on different occasions, being subject to a temperature correction for the density of mercury and for the expansion of the iron rod. The correction is given in the fifth column, and the weights that would have been required, had the temperature been 15°, in the sixth. The numbers in the second and sixth columns should agree, but they are liable to a discontinuity when the tap is re-greased.

In deducing the weight of the gas we compare each weighing "full" with the mean of the preceding and following weights "empty," except in the case of October 15, when there was no subsequent weighing empty. The results are given in the Table (see top of next column).

There is here no evidence of the variation in the density of air suspected by Regnault and v. Jolly. Even if we include the results for September 27th, obviously affected by irregularity in the weights of the globe empty, the extreme difference is only 0.4 m.grm., or about $\frac{1}{8000}$ th part.

September 27	2.37686
" 29	2.37651
October 3	2.37653
" 8	2.37646
" 11	2.37668
" 13	2.37679
" 15	2.37647
Mean..	2.37661

To allow for the contraction of the globe (No. 14) when weighed empty, discussed in my former papers, we are to add 0.00056 to the apparent weight, so that the result for air becomes—

2.37717.

This is the weight of the contents at 0° and under the pressure defined by the manometer gauge at 15° of the thermometer. The reduction to standard conditions is, for the present, postponed.

Oxygen.

This gas has been prepared by three distinct methods (a) from chlorates, (b) from permanganate of potash, (c) by electrolysis.

In the first method, mixed chlorates of potash and soda were employed, as recommended by Shenstone, the advantage lying in the readier fusibility. The fused mass was contained in a Florence flask, and during the wash out was allowed slowly to liberate gas into a vacuum. After all air had been expelled, the regulating tap was closed, and the pressure allowed gradually to rise to that of the atmosphere. The temperature could then be pushed without fear of distorting the glass, and the gas was drawn off through the regulating tap. A very close watch over the temperature was necessary to prevent the evolution of gas from becoming too rapid. In case of excess, the superfluous gas was caused to blow off into the atmosphere, rather than risk imperfect action of the potash and phosphoric anhydride. Two sets of five fillings were effected with this oxygen. In the first set (May, 1892) the highest result was 2.6272, and the lowest 2.6266; mean, 2.62691. In the second set (June, July, 1892) the highest result was 2.6273, and the lowest 2.6267, mean 2.62693.

The second method (b) proved very convenient, the evolution of gas being under much better control than in the case of chlorates. The re-crystallised salt was heated in a Florence flask, the wash-out, in this case also, being facilitated by a vacuum. Three fillings gave satisfactory results, the highest being 2.6273, the lowest 2.6270, and the mean 2.62714. The gas was quite free from smell.

By the third method I have not as many results as I could have wished, operations having been interrupted by the breakage of the electrolytic generator. This was, however, of less importance, as I had evidence from former work that there is no material difference between the oxygen from chlorates and that obtained by electrolysis. The gas was passed over hot copper, as detailed in previous papers. The result of one filling, with the apparatus as here described, was 2.6271. To this may be added the result of two fillings obtained at an earlier stage of the work, when the head of the manometer was exhausted by an independent Sprengel pump, instead of by the Töppler. The value then obtained was 2.6272. The results stand thus:—

Electrolysis (2), May, 1892	2.6272
" (1), "	2.6271
Chlorates (5), May, 1892	2.6269
" (5), June, 1892	2.6269
Permanganate (3), January, 1893	2.6271
Mean..	2.62704
Correction for contraction	0.00056
				2.62760

It will be seen that the agreement between the different methods is very good, the differences, such as they are, having all the appearance of being accidental. Oxygen prepared by electrolysis is perhaps most in danger of being light (from contamination with hydrogen), and that from chlorates of being abnormally heavy.

Nitrogen.

This gas was prepared, in the usual manner, from air by removal of oxygen with heated copper. Precautions are required, in the first place, to secure a sufficient action of the reduced copper, and, secondly, as was shown by v. Jolly, and later by Leduc, to avoid contamination with hydrogen which may be liberated from the copper. I have followed the plan, recommended by v. Jolly, of causing the gas to pass finally over a length of unreduced copper. The arrangements were as follows:—

Air drawn through solution of potash was deprived of its oxygen by reduced copper contained in a tube of hard glass heated by a large flame. It then traversed a U-tube, in which was deposited most of the water of combustion. The gas, practically free, as the event proved, from oxygen, was passed, as a further precaution, over a length of copper heated in a combustion furnace, then through strong sulphuric acid,* and afterwards back through the furnace over a length of oxide of copper. It then passed on to the regulating tap, and thence through the remainder of the apparatus, as already described. In no case did the copper in the furnace, even at the end where the gas entered, show any signs of losing its metallic appearance.

Three results, obtained in August, 1892, were—

August 8.. ..	2'31035
„ 10.. ..	2'31026
„ 15.. ..	2'31024
Mean	2'31028

To these may be added the results of the two special experiments made to test the removal of hydrogen by the copper oxide. For this purpose a small hydrogen generator, which could be set in action by closing an external contact, was included between the two tubes of reduced copper, the gas being caused to bubble through the electrolytic liquid. The quantity of hydrogen liberated was calculated from the deflection of a galvanometer included in the circuit, and was sufficient, if retained, to alter the density very materially. Care was taken that the small stream of hydrogen should be uniform during the whole time (about 2½ hours) occupied by the filling, but, as will be seen, the impurity was effectually removed by the copper oxide.† Two experiments gave—

September 17	2'31012
„ 20	2'31027
Mean	2'31020

We may take as the number for nitrogen—

	2'31026
Correction for contraction ..	56
	2'31082

Although the subject is not yet ripe for discussion, I cannot omit to notice here that nitrogen prepared from ammonia, and expected to be pure, turned out to be decidedly lighter than the above. When the oxygen of air is burned by excess of ammonia, the deficiency is about 1/1000th part.‡ When oxygen is substituted for air,

* There was no need for this, but the acid was in position for another purpose.

† Much larger quantities of hydrogen sufficient to reduce the oxide over several centimetres, have been introduced without appreciably altering the weight of the gas.

‡ *Nature*, vol. xvi., p. 512.

so that all (instead of about one-seventh part) of the nitrogen is derived from ammonia, the deficiency of weight may amount to ½ per cent. It seems certain that the abnormal lightness cannot be explained by contamination with hydrogen, or with ammonia, or with water, and everything suggests that the explanation is to be sought in a dissociated state of the nitrogen itself. Until the questions arising out of these observations are thoroughly cleared up, the above number for nitrogen must be received with a certain reserve. But it has not been thought necessary, on this account to delay the presentation of the present paper, more especially as the method employed in preparing the nitrogen for which the results are recorded is that used by previous experimenters.

(To be continued).

ON THE DETERMINATION OF IODINE IN HALOID SALTS BY THE ACTION OF ARSENIC ACID.*

By F. A. GOOCH and P. E. BROWNING.

THREE years ago we demonstrated (*American Journal of Science*, xxxix., p. 188) the possibility of determining iodine in mixtures of alkaline chlorides, bromides, and iodides, with rapidity and exactness, by taking advantage of the behaviour of arsenic acid toward the haloid salts in presence of sulphuric acid of definite strength. We showed in brief that when amounts of potassium iodide ranging from 0.005 grm. to 0.5 grm. were dissolved in 100 c.m.³ of water containing 2 grms. dihydrogen potassium arseniate and 20 c.m.³ of a mixture of sulphuric acid with water in equal volumes, the entire amount of iodine was expelled on boiling down the solution from 100 c.m.³ to 35 c.m.³; and further, that arsenic, reduced to the arsenious condition to an amount the exact equivalent of the iodine liberated, remained in solution and was determinable, after neutralisation of the acid, in presence of an alkaline bicarbonate, by titration against standard iodine according to Mohr's classical method. We studied carefully the behaviour of alkaline bromides and chlorides under identical conditions, and determined that 0.5 grm. of potassium bromide acted upon the mixture of arseniate and acid to the extent of reducing arsenic equivalent to 0.0008 grm. of iodine, and that 0.5 grm. of sodium chloride did not reduce arsenic, but did cause, under the conditions, a volatilisation proportional to the amount of arsenious oxide present, the loss amounting at the most—when 0.56 grm. of the iodide was present to exert its reducing action upon the arsenic—to 0.0011 grm. We showed, furthermore, that these maximum errors, due to the action of bromides and chlorides, though not large and tending to neutralise one another when both bromides and chlorides are present, may be eliminated by the application of a numerical correction to the results whenever the amounts of bromide and chloride present become known.

Recently Messrs. Friedheim and Meyer (*Zeitsch. f. Anorg. Chem.*, i., p. 407) have recognised the value of our reaction, and applied it to the elimination of iodine from mixtures of haloid salts. They have, however, taken issue with us (unadvisedly, as we think) as to matters of detail. They have, in the first place, put themselves upon record as being unable to titrate arsenious oxide by iodine in alkaline solution under the conditions of our process. They account for their failure by the wholly unsupported hypothesis that the iodine reaction is unavailable in presence of the amounts of salts present, and modify the treatment by distilling, collecting the iodine in the distillate, and determining it by the thiosulphate method, thus introducing complexity of

* *American Journal of Science*, xlv., April, 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

apparatus and manipulation, and sacrificing the simplicity and rapidity which are chief advantages of our process. Had they read our paper with intelligent care it must have been evident that we had given special attention to the question of the influence of the salts present upon the iodine reaction; for we expressly stated that "due correction was made for the amount of iodine necessary to develop the test-colour in a solution prepared and treated similarly in all respects to the experimental solutions excepting the introduction of the iodide—the correction amounting to a single drop more of the decinormal iodine than was required to produce the end reaction in the same volume of pure water containing only the starch indicator." It is obvious that such errors as 0.003 to 0.006 grm., which Messrs. Friedheim and Meyer found even in the absence of bromides and chlorides, are not explicable by the action of the salts which we used. Our errors ranged under like conditions from 0.0009 grm. — to 0.0003 grm. +, with a mean error in nine determinations of 0.0002 grm. —.

Everybody knows that the starch iodide test is most delicate in acid solutions and in presence of combined iodine, but Mohr's method of titrating arsenious oxide and iodine against one another in alkaline solution is sufficiently delicate for very exact work, provided only that the alkali in excess is in the form of the bicarbonate, that the starch emulsion is used in abundance, and that the volumes of solutions titrated are regulated to low and uniform measure. In many determinations of iodine made by our method at different times and with different materials, it has never been our ill-fortune to chance upon results so extraordinary as those of Messrs. Friedheim and Meyer, though we have met in the course of our work with potassium arseniate so contaminated with nitrates as to be unfit for use and with alkaline hydroxides too impure to employ. Most analytical processes depend for their exactness upon the use of proper materials; ours is no exception to the rule in this regard.

As to the correctness of the main reaction there appears to be no difference of opinion between Messrs. Friedheim and ourselves. We have, therefore, taken the pains, perhaps unnecessarily, to make experiments in which the estimation of the iodine of the same identical portions is effected both in the distillate and in the residue, in order that the two modes of estimation may be brought into direct comparison. It is scarcely needful to add that we took care to work with pure reagents. The potassium iodide, like that which we employed in our former investigation, was prepared by acting with re-sublimed iodine upon an excess of iron wire, pouring off the solution from the iron when the colour of iodine had vanished, adding iodine equal to one-third the amount of that originally used, pouring the filtered liquid into a boiling solution of the calculated equivalent of potassium carbonate (from the bicarbonate), and filtering off the precipitated magnetic oxide of iron. The slightly alkaline solution thus made, containing approximately 2 grms. of potassium iodide in 100 c.m.³, and free from chlorine and bromine, was standardised by precipitating the iodine from weighed portions in the form of silver iodide and weighing upon asbestos. The other reagents—the sulphuric acid, the sodium hydroxide, the acid potassium carbonate, the dihydrogen potassium arseniate—when present in the proportions used in our process and mixed with 5 c.m.³ of clear starch solution prepared by Gastine's formula (*Bull. Soc. Chim.*, 1., 172) (5 grms. starch, 0.01 HgI₂, 1 litre of water) gave the starch blue with a single drop of decinormal iodine at all dilutions below 300 c.m.³. The results of these experiments are given in the accompanying Table.

Experiments 1 to 4 were made exactly in accordance with the directions of our former paper, the mixtures being simply boiled in an Erlenmeyer flask trapped to prevent mechanical loss by hanging in the neck of the flask, with the larger end downward, a straight, two-bulbed drying tube cut off so as to leave the larger tube

	Iodine taken in form of KI. Grm.	Iodine found in residue by our method. Grm.	Iodine found in distillate by As ₂ O ₃ . Grm.	Iodine found in distillate by Na ₂ S ₂ O ₃ . Grm.	Error in residue. Grm.	Error in distillate. Grm.
1.	0.4054	0.4052	—	—	0.0002 —	—
2.	0.4057	0.4055	—	—	0.0002 —	—
3.	0.4054	0.4052	—	—	0.0002 —	—
4.	0.4054	0.4052	—	—	0.0002 —	—
5.	0.4042	0.4046	0.4046	—	0.0004 +	0.0004 +
6.	0.4050	0.4052	0.4040	—	0.0002 +	0.0010 —
7.	0.4050	0.4052	—	0.4039	0.0002 +	0.0011 —
8.	0.4058	0.4052	—	0.4051	0.0006 —	0.0007 —
9.	0.4054	0.4046	—	0.4051	0.0008 —	0.0003 —
10.	0.4042	0.4046	—	0.4039	0.0004 +	0.0003 —
11.	0.4055	0.4052	—	0.4057	0.0003 —	0.0002 +

about 4 c.m. in length. These four experiments all gave the same result, which differed from the theory by 0.0002 grm. —. The mixtures of the remaining experiments were treated in a flask connected with a cooled receiver and absorption tubes for condensing the distilled iodine (all joints being of glass and carefully ground), and carbon dioxide was passed through the apparatus in slow current to facilitate the transfer of iodine and quiet boiling. In experiments 5 and 6 the iodine was received in an alkaline solution of standard arsenious oxide, and titration was effected with standard iodine after addition of starch. The residue was treated by our method. It will be observed that the residues, which contain the large amounts of salts, yield results by titration practically identical with those obtained by treating the distillates which do not contain the large masses of salts. In experiments 7 to 11 the iodine distilled was received in potassium iodide and estimated by standard sodium thiosulphate, itself standardised against the iodine whose value in terms of the standard arsenious oxide was also known. The residues were treated by our method. It is evident that the errors of both processes of treatment are reasonably small (respectively 0.0001 grm. — and 0.0004 grm. — in the average), with what difference there is in favour of our treatment of the residues. Our process is incomparably the more convenient and rapid. We do not doubt that Messrs. Friedheim and Meyer could have obtained equally good results had they worked with pure reagents.

Messrs. Friedheim and Meyer disagree with us also as to the degree of concentration of the liquid necessary to insure the complete expulsion of iodine, and as to the effect of the concentration upon bromides present—points to which we gave particular attention in our former paper. We showed that, in general, upon boiling a mixture of iodide with sulphuric acid, and the arseniate diluted with water, the amount of iodine removed depended upon the proportion of the sulphuric acid to the final volume of the whole liquid, it being plainly shown that even after the liquid had lost the colour of free iodine in the process of concentration, it was still possible to detect combined iodine. Further concentration and, to some extent, dilution and repetition of the concentration to the former point tend to set free the residual iodine.

In experimenting upon the proportions of acid most convenient for the work, we found that a solution made up to contain 0.5 grm. of potassium iodide, 2 grms. of dihydrogen potassium arseniate, and 20 c.m.³ of the sulphuric acid mixture (1:1 by volume) retained when boiled down to 40 c.m.³ no determinable free iodine, and but the faintest trace of combined iodine, while at 35 c.m.³ the liquid was free from iodine in any form. Upon experimenting as to the behaviour of mixtures of chlorides and iodides, we found that 0.5 grm. of sodium chloride added to the mixture containing 0.5 grm. of the iodide occasioned at 40 c.m.³ a maximum loss of arsenious chloride equivalent to 0.0004 grm. of the oxide, or to 0.0008 grm. at 30 c.m.³; and that the loss as a matter of course is less as the amount of iodide present (and consequently the arsenious oxide formed) is diminished,

We found that 0.5 gm. of potassium bromide treated in similar manner occasioned no loss of arsenious bromide, but did induce at 35 c.m.³ reduction of the arsenic acid amounting to 0.0005 gm. of iodine. Smaller amounts of bromide produced proportionately smaller effects, but concentration even a little below 35 c.m.³ was likely to be productive of serious error. We fixed upon 35 c.m.³, therefore, as the ideal concentration for removing iodine from unknown mixtures with chlorides and bromides, but expressly stated that failure to concentrate below 40 c.m.³ introduces no appreciable error, while great care should be taken not to press the concentration below 35 c.m.³ on account of the danger of bringing about the reduction of the arsenic by the bromide.

Messrs. Friedheim and Meyer contend that the reduction of volume under the conditions should not be pressed beyond 50 c.m.³ at the most, and cite in proof experiments in which potassium bromide in amounts less than half as great as those which we used caused an error on concentration to 35 c.m.³, equivalent to five or six milligrams of iodine. They recommend boiling from 150—50 c.m.³ to remove the iodine without disturbing bromine. Our former experiments are sufficiently definite upon these points. We have, however, determined directly and quantitatively the amounts of iodine remaining unexpelled when solutions are boiled from 150—50 c.m.³ and found, in certain experiments, in which the additional iodine expelled in concentrating from 50—35 c.m.³ was collected in potassium iodide and estimated with sodium thiosulphate, that about 0.0013 gm. remained when 0.5 gm. of potassium iodide was originally taken, and 0.0003 gm. when 0.25 gm. of the iodide was present at the first. It is evident, therefore, that concentration to 50 c.m.³ is not sufficient when the maximum amount of iodide may be present. We have also made certain experiments—recorded below—in which the bromine liberated at different degrees of concentration was collected in potassium iodide and estimated by the iodine set free. In our former work we inferred the loss of bromine from the effects upon the arsenic acid in the residues. In these experiments solutions of potassium bromide (free from iodine), with 20 c.m.³ of sulphuric acid (1:1), and 2 grms. of dihydrogen potassium arseniate were boiled down in a flask connected by ground glass joints with a cooled receiver containing potassium iodide, and the iodine set free was estimated by standard sodium thiosulphate.

KBr taken. Grm.	Initial volume. C.m. ³	Final volume. C.m. ³	Bromine in distillate. Grm.
0.5	150	50	trace
	50	40	trace
	40	35	0.0004
0.5	50	31	0.0010
	31	26	0.0064
	26	23	0.0072
	45	40	none
0.25	40	31	0.0004
	31	27	0.0010
0.25	50	35	0.0003
0.1	50	30	0.0003

From these results, which confirm very closely those obtained by an examination of the residues and recorded in our former paper, it is evident that the concentration may go under the most unfavourable conditions—when the maximum amount of bromide is present—to 40 c.m.³ without loss and to 35 c.m.³ with small loss. As we stated in our former paper, concentration below 35 c.m.³ should be avoided.

In our former paper we showed that the iodine could be determined in unknown mixtures of sodium chloride, potassium bromide, and potassium iodide taken in amounts not exceeding 1.5 gm. (in which, however, neither individual salt was present in amount exceeding 0.5 gm.) with a maximum error ranging from 0.0013

gm. — to 0.0016 gm. +. We showed, further, that when the amounts of chloride and bromide present were known also, a correction for the action of these salts might be applied, which reduced the maximum errors to 0.0010 gm. — and 0.0008 gm. +, and gave a mean error of 0.0001 gm. — for twenty-six determinations.

In conclusion, we affirm the correctness of our former work, and reiterate our former directions without change.

NOTICES OF BOOKS.

Practical Treatise on Chemical Analysis and Toxicological Researches (Traite Pratique d'Analyse Chimique et de Recherches Toxicologique). By G. GUERIN, Professor attached to the Faculty of Medicine at Nancy. Paris: Georges Carré, 1893. 8vo., pp. 492.

THIS work possesses certain very valuable features. In the first section on preliminary trials by the dry way there are a series of tables showing the colouration of borax beads obtained before the blowpipe with the metallic oxide, whilst a similar table shows the reactions obtained with phosphorus salt.

The third part treats of the distinctive characters of different bodies, and gives—at least, where the rarer elements are concerned—the spectroscopic reactions of the substances in question. We notice that in this part the metals are arranged not in their analytical groups, but alphabetically. The non-metallic substances are entitled *more gallico* metalloids. The organic salts, *e.g.*, uric, hippuric, phenic, meconic, &c., are noticed more fully than we generally find in text-books of moderate size.

In addition to the notes on the spectral reactions of the metals, there is a part exclusively devoted to spectral analysis. Here we find a catalogue of the rays of the most important bodies expressed in wave-lengths, figures of different spectroscopes, an account of emission spectra, of the manner of producing spectrum lines, observing and measuring them, the projection of spectra, the use of the electric spark, on absorption spectra, and the manner of their observation.

We find here the interesting fact recorded by M. de Chardonnet that certain persons who had undergone the operation for cataract, *i.e.*, had been deprived of the "crystalline," saw the spectrum prolonged far beyond the violet, which forms the ordinary limit of the visible portion. Physicists explain this phenomenon by assuming that the radiations neither of the extreme red nor of the ultra-violet reach the retina. The aqueous media of the eye would absorb the infra red rays, as does water, and the tissue of the crystalline being fluorescent, absorb the ultra-violet rays, as do all substances which possess this property.

After instructions for observing the absorption spectra and an account of the absorption bands of chlorophyll, of potassium permanganate, and of the salts of didymium and erbium, the author proceeds to describe and figure the characteristic bands of blood. Here the name of Sir G. Stokes is converted into Stockes. A special chapter is devoted to the detection of blood spots. Here mention is made of the "hæmato spectroscope" of M. de Thierry.

Part VI. is devoted to toxicology, prominence being given to arsenic, phosphorus, hydrocyanic acid, chloroform and chloral, and the alkaloids. The methods of Stas and Dragendorff are explained and criticised at length. Next follow the bacterian alkaloids, the ptomaines, and leucomaines. We may here ask whether the time has yet come for the authoritative promulgation of structural formulæ for these bodies? Are they, even if capable of demonstration, in their right place in an analytical treatise?

The reactions of the ordinary alkaloids are fully laid

down. The venoms of serpents are mentioned in passing as containing alkaloids, but we do not find any detailed critical description. Much research is here still required, but it cannot be undertaken in Britain, or, indeed, in any part of the British Empire, on account of the agitation stirred up by the bestiarists.

From the alkaloids Prof. Guérin passes to the analysis of potable waters. He admits the faintly blue colour of pure waters if seen in deep masses. He rightly condemns magnesium waters, but he holds that the chemico-physical analysis of waters does not warrant a decision on their hygienic properties without a biological examination.

In the chemical analysis of waters he retains the unsatisfactory procedure of evaporating to dryness at 100° and noting the loss on ignition at a red heat. The shortcomings of this procedure are so well known that they do not need to be here recapitulated. Ammonia and organic nitrogen he determines by Wanklyn's method. For nitrates he gives the methods with brucine, with diphenylamine, and with the sulphophenic reagent of Grandval and Lajoux. We are surprised to find no reference to lead, one of the most dangerous and commonest impurities in potable waters.

The bacteriological examination of drinking-waters is discussed very fully, but there is no reference to the analysis of sewage, of industrial waste-waters, drainage, or urines. Lastly come instructions for the assay of clays and of irons and steels.

Prof. Guérin's work is upon the whole highly useful, very rich in some directions, though strangely defective in others.

Diseases Incident to Workpeople in Chemical and other Industries. An Address Delivered before the Chemical and Physical Society of University College, London.
By WATSON SMITH. London: Eyre and Spottiswoode, 1893. 8vo., 34 pp. (Second Notice.)

THE match-manufacture employs a small number of persons in comparison with the production of alkali, but it must be charged with a much higher proportion of mischief. The manufacture of phosphorus itself is less dangerous than its subsequent elaboration into matches. The special disease which may be produced is necrosis of the jaw. At the works of Messrs. Albright and Wilson, of Birmingham, the largest phosphorus makers in the world, every known precaution for the safety of the workpeople is taken and with success. No girls or young boys are employed, and the cases of necrosis occurring are few, and being at once attended to they are easily cured. The firm state that men of a scrofulous taint or of intemperate habit are most susceptible to the mischief.

In match-making the risk is greater. The number of hands is larger, the phosphorus is much sub-divided, and has consequently much greater opportunity of giving off its vapours. There is a remedy, the exclusive use of the so-called red or amorphous phosphorus in place of the normal white or yellow form. In some countries the use of the latter kind is legally prohibited. But such enactments are too often a dead letter even in Germany, where, according to Prof. Lunge, it is carried on secretly, and will be so until the small match-works,—the so-called house factories—are stopped. Such establishments are much less rampant in England. In Switzerland the match-manufacture is about to be constituted a Government monopoly on purely sanitary grounds. In the small Swiss factories it has actually been customary for the workmen to be paid partly in money and partly in matches, reckoned at 30 per cent above their real value!

It is stated, on the authority of the *Chemiker Zeitung*, that the attempts to supersede phosphorus altogether in the match-manufacture have, so far, proved a failure, the matches thus made being too explosive. Perhaps, however, the difficulty may yet be overcome, which is very desirable, since all the phosphorus in existence is wanted as plant-food.

Mr. Watson Smith tells us that in the safety-match department of Messrs. Bryant and May no smell of phosphorus could be recognised. The match-works of the Salvation Army use only amorphous phosphorus and keep up thorough ventilation. The health of the workpeople is satisfactory.

White-lead next claims our attention. Mr. Watson Smith rightly contends that whatever process is used in this manufacture, so long as there is dust there is danger. Even the new white-lead, consisting principally of lead sulphate, cannot be absolutely safe. Lead sulphate is decidedly soluble in ammonium acetate and tartrate, and it is converted into lead carbonate by sodium bicarbonate. Hence, if a person is exposed to the dust of lead sulphate, a draught of the ordinary effervescing beverages may at once produce in his digestive organs the actively poisonous lead carbonate.

We hope that the author's protest against dilute sulphuric acid as a safeguard against lead poisoning will not be generalised so as to form an objection to its use as a prophylactic against cholera and various other tropical diseases,—of course not including yellow fever, the bacillus of which seems to thrive in acid media.

It appears that "workmen employed in factories where arsenic acid and also bichromate of potash are made, especially the former, are subject to blisters and ulcers that precisely resemble those common in syphilitic diseases. The result is that such workmen have often been treated, and wrongly treated, for acute syphilis." It is satisfactory that the demand for arsenic acid has much abated since the Medlock process is no longer exclusively used in the manufacture of magenta.

Carbon disulphide, when inhaled, is a serious poison, and it is the more formidable as its effects have been wrongly ascribed to alcoholic intoxication. Mr. H. L. Terry, a former pupil of the author, has hopes that in the process for vulcanising indiarubber it may soon be superseded by a newly discovered product.

Dr. Weber, of Manchester, gives a simple method of distinguishing the earlier stages of poisoning by carbon disulphide from the effects of alcohol.

The patient is placed in the open air for from five to ten minutes, and is allowed to drink some milk and soda-water. If alcohol has been at work no improvement is perceived, but in the case of carbon disulphide the symptoms disappear very rapidly. It is to be noted that though the "curing" of caoutchouc goods is now conducted in machines, encased and well ventilated, yet "the men attending them frequently carelessly expose themselves to the carbon disulphide vapours escaping in large quantities."

Two tests are here laid down for detecting carbon disulphide in saliva. For the *phenylhydrazine* reaction from 10—15 c.c. of the saliva are shaken up with from 20—25 c.c. of benzene. All the CS₂ is taken up by the latter, and on adding to it a few crystals of phenylhydrazine (the free base), a beautiful crop of the crystalline compound is deposited.

The triethylphosphine reaction is obtained by shaking up the saliva with an ethereal solution of triethylphosphine, P(C₂H₅)₃. If CS₂ is present a beautiful pink colour appears, due to the formation (C₂H₅)₃P·CS₂. If the quantity of CS₂ is not too small, a red crystalline deposit of the compound is obtained. According to Dr. Weber, the chief danger from nitrobenzene lies not so much in the preparation of this compound, or in its conversion into aniline, as in the manufacture of metanilic acid and benzidine. It may be pronounced a treacherous poison, as its symptoms appear suddenly and without any warning. Dr. Weber himself seems to have had a rather narrow escape from poisoning by the vapours of aniline.

Cases of arsenical poisoning occur at pigment-works in the manufacture of Schweinfurt green (or Paris green, as it is sometimes called) and of "rose pink"—a preparation of magenta precipitated upon aluminium arsenite.

The proposal to constitute a small consultative committee to advise the Home Secretary on the sanitary bearings of various trades, *if rightly constituted*, would be exceedingly useful.

Mr. Watson Smith's work will, we hope, be widely read and appreciated. It will be a safe guide for journalists.

Electro-Medical Supplies. The General Electric Co., Limited, Queen Victoria Street, London.

This catalogue figures and describes an extensive assortment of apparatus for *bona fide* medical and surgical purposes. Practitioners will note here the absence of those alleged wonder-working batteries which have been so much pushed of late by persons scantily acquainted either with electricity or pathology.

A Summer School of Art and Science. Edinburgh Summer Meeting. Seventh Session, July 31st to August 26th, 1893.

It is satisfactory to find that this movement promises to be permanent. In the remarks on the "educational purpose of the courses," we note the following passage with especial satisfaction: "Hence the examination method is here definitely abandoned; a keener stimulus, even a more satisfactory test of progress, being found in accustoming the student to take part in his own education." Or, again, "the student is regarded, not as a receptacle for information, but as a *possible producer of independent thought*." The attempt is made "not merely to offer a series of special courses, each of adequate thoroughness, but to keep up, as far as possible, a parallelism of treatment and to co-ordinate these parallel courses into a larger whole." To such endeavours we can merely wish the most ample success.

We trust, however, that the "humanities" will not be allowed to encroach too far on the time and attention of the school, as they have a tendency to do in Britain. We have great confidence in the guidance of Professor Geddes.

Incandescence Lamps. Price List. The Edison and Swan United Electric Light Company, Limited, Section I.

Electric Light Installation Fittings. Price List. The Edison and Swan United Electric Light Company, Limited, Section II.

Electric Light Measuring Instruments. The Edison and Swan United Electric Light Company, Limited, Section III.

THESE copious illustrated price lists will be exceedingly useful for municipal authorities who may be contemplating the introduction, extension, or improvement of an electric light installation.

It is to be hoped that the instruments used for measuring electric current as supplied to consumers will prove in practice more trustworthy than the gas-meter, which has earned for itself the unenviable name of the "mechanical Ananias."

CORRESPONDENCE.

OXIDATION PRODUCTS OF GLUCOSE.

To the Editor of the Chemical News.

SIR,—Will any of your readers kindly inform me of the oxidation products of glucose when treated with Fehling's solution? The text-books on analysis (Sutton, Blyth, &c.) are satisfied with the statement that Cu_2O is formed by reduction and overlook the rest of the reaction. It

certainly seems surprising that the chemistry of so important a process should receive so little attention.—I am, &c.,

A. C. LANGMUIR.

School of Mines, Columbia College,
New York.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 15, April 10, 1893.

Volatility of Manganese.—S. Jordan.—The author's former researches have been confirmed by H. H. Lorenz and Heusler, who conclude that manganese, unlike nickel and iron, does not react with carbon monoxide, and that it is volatilised as a metal, at little above its point of fusion.

Determination of Atomic Weights by the Method of Limit.—G. Hinrichs.—The author finds that for each atom of the unique and primitive matter contained in hydrogen there are exactly sixteen in the atom of oxygen.

Nitro-Copper.—Paul Sabatier and J. R. Senderens.—This compound is obtained by reducing cupric oxide and directing upon the metal thus procured, at 25° or 30° , vapours of nitrogen peroxide. The compound may be represented by the formula Cu_2NO_2 . It is stable in dry air in the cold, but it is decomposed by temperatures exceeding 90° . It reacts violently with water.

Isomerism of the Amido-Benzoic Acids.—Oechsner de Coninck.—The author has pursued the comparative study of the three amido-benzoic acids, determining their solubility in neutral solvents such as pure alcohol and ether, methylic alcohol, acetone, methyl and ethyl iodides, chloroform, bromoform, oil of turpentine, and distilled water at different temperatures.

Phthalocyanacetic Ether.—P. Th. Müller.—This paper does not admit of useful abridgment.

Observations on a Series of Novel Forms of Snow, collected at very Low Temperatures.—Gustav Nordenskiöld.—These snow-flakes seem a connecting-link between the geometrical forms of dead nature, bounded by plane surfaces and the curved and rounded forms of organised beings.

Zeitschrift für Analytische Chemie.
Vol. xxxii., Part 2, 1893.

Simple Separation of Iron and Alumina.—H. Bonträger.—Both hydroxides are precipitated together, ignited, and weighed as oxides. They are then re-dissolved in hydrochloric acid, rendered almost neutral with potassa-lye—not soda—and both oxides are then precipitated with neutral liquid potash soap, as sold by A. Keysser, of Hanover, or A. Gude, of Leipzig. The precipitation must be effected in heat, and an excess of soap must in any case be avoided, as the oleates are otherwise re-dissolved. It is filtered through a filter moistened with hot water, and washed with hot water until the potassium chloride is removed. The filter is then partially dried over calcium chloride until the bulk of the water is removed. The gelatinous mass is then treated with hot petroleum until it runs off colourless, and consequently all iron oleate has passed into solution. The filter is burnt, and the residual porous snow-white alumina is weighed. As a precaution, the petroleum solution may be burnt and incinerated so as to weigh the iron oxide. Ferrous oxide may be separated from alumina in this manner without previous oxidation.

Rapid Reduction of Potassium Platinum Chloride.—H. Bornträger.—The compound is dissolved in boiling water, and the platinum is precipitated by liquid potash soap. It falls to the bottom as a smeary and sandy light-coloured clot. The supernatant solution is decanted off, and the clot (which consists of a double salt of potassium chloride and platinum oleate), is ignited in a porcelain crucible. Thus, in a few minutes we obtain a very effective platinum-black, which is freed from potassium chloride by washing with hot water. The clot, on ignition, leaves 42 per cent residue with 23 per cent platinum.

Separation of Strontium and Calcium.—Prof. R. Fresenius.—The author, as the final result of his prolonged investigations, concludes that only the method of H. Rose, as improved by F. Stromeyer, can be recommended for a true separation.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. viii., No. 86.

Use of the Safety-Lamp for the Detection of Inflammable Vapours.—Frank Clowes.—(From the CHEMICAL NEWS).

MISCELLANEOUS.

The Institute of Chemistry of Great Britain and Ireland.—An Extraordinary General Meeting was held at 30, Bloomsbury Square, London, W.C., on Thursday, the 27th April, 1893, for the following purposes, viz.:—I.—To pass the following resolution: "That the Council be empowered to expend a sum not exceeding £1000 upon the erection of a building to be used as a laboratory, upon the ground at the back of the house at 30, Bloomsbury Square." II.—To consider the Report of the Censors, and pass a resolution, or resolutions, thereon.

Report of the Censors.—"The Censors having received information which tends to show that practices of an unprofessional character are unduly prevalent among practising analytical chemists, desire to draw the attention of the Council to the necessity for establishing among the members of the Institute more definitely than at present a standard of conduct in a professional sense comparable with that which is recognised in the professions of law and medicine. They therefore recommend that at the next conference, which should be summoned as an extraordinary general meeting in accordance with Bye-law 5, the following resolutions shall be submitted: I.—That the following acts or any of them shall be held to be 'discreditable to the profession of analytical and consulting chemist,' viz.: (1) Advertising for practice in newspapers, journals, magazines, or other published papers. (2) Sending out by post or otherwise letters, circulars, or cards, offering professional services. (3) Undertaking through another person or agency the performance of professional work at fees representing only a small fraction of the usual recognised scale of fees for analytical work. (4) Supplying to other persons, not being qualified chemists, reports upon samples or processes with the knowledge that these other persons will issue such reports as their own work. (5) Issuing or allowing to be issued certificates of purity or superiority concerning advertised commodities, such certificates being either not based upon the results of an analysis, or containing exaggerated, irrelevant, or merely laudatory expressions, designed to serve the purposes of a trade puff. (6) The unauthorised use of letters indicating University degrees. II.—That in the opinion of this meeting the Council will be justified in regarding these acts as offences of the kind referred to in the Charter (chap. 16, 3) as discreditable to the profession of analytical and consulting chemist."

tical and consulting chemist.—Signed this First day of December, 1892, WILLIAM A. TILDEN (*Chairman*), J. BELL, CHARLES E. CASSAL, E. FRANKLAND, T. E. THORPE (*Censors*)."

Smithsonian Institution.—Circular Concerning the Hodgkins Fund Prizes.—In October, 1891, Thomas George Hodgkins, Esq., of Setauket, New York, made a donation to the Smithsonian Institution, the income from a part of which was to be devoted "to the increase and diffusion of more exact knowledge in regard to the nature and properties of atmospheric air in connection with the welfare of man." With the intent of furthering the donor's wishes, the Smithsonian Institution now announces the following prizes to be awarded on or after July 1, 1894, should satisfactory papers be offered in competition:—

1. A prize of 10,000 dollars for a treatise embodying some new and important discovery in regard to the nature or properties of atmospheric air. These properties may be considered in their bearing upon any or all of the sciences,—e.g., not only in regard to Meteorology, but in connection with hygiene, or with any department whatever of biological or physical knowledge.

2. A prize of 2000 dollars for the most satisfactory essay upon: (a) The known properties of atmospheric air considered in their relationships to research in every department of natural science, and the importance of a study of the atmosphere considered in view of these relationships. (b) The proper direction of future research in connection with the imperfections of our knowledge of atmospheric air, and of the connections of that knowledge with other sciences. The essay as a whole should tend to indicate the path best calculated to lead to worthy results in connection with the future administration of the Hodgkins foundation.

3. A prize of 1000 dollars for the best popular treatise upon atmospheric air, its properties and relationships (including those to hygiene, physical and mental). This essay need not exceed 20,000 words in length; it should be written in simple language, and be suitable for publication for popular instruction.

4. A medal will be established, under the name of the Hodgkins Medal of the Smithsonian Institution, which will be awarded annually or biennially, for important contributions to our knowledge of the nature and properties of atmospheric air, or for practical applications of our existing knowledge of them to the welfare of mankind. This medal will be of gold, and will be accompanied by a duplicate impression in silver or bronze.

The treatises may be written in English, French, German, or Italian, and should be sent to the Secretary of the Smithsonian Institution, Washington, before July 1, 1894, except those in competition for the first prize, the sending of which may be delayed until December 31, 1894. The papers will be examined, and prizes awarded, by a committee to be appointed as follows:—One member by the Secretary of the Smithsonian Institution, one member by the President of the National Academy of Sciences, one by the President, pro tem., of the American Association for the Advancement of Science; and the committee will act, together with the Secretary of the Smithsonian Institution as member, ex officio. The right is reserved to award no prize if, in the judgment of the committee, no contribution is offered of sufficient merit to warrant an award. An advisory committee of not more than three European men of science may be added at the discretion of the Committee of Award. If no disposition be made of the first prize at the time now announced, the Institution may continue it until a later date, should it be made evident that important investigations relative to its object are in progress, the results of which it is intended to offer in competition for the prize. The Smithsonian Institution reserves the right to limit or modify the conditions for this prize after December 1, 1894, should it be found necessary. Should

any of the minor prizes not be awarded to papers sent in before July 1, 1894, the said prizes will be withdrawn from competition. A principal motive for offering these prizes is to call attention to the Hodgkins Fund, and the purposes for which it exists, and accordingly this circular is sent to the principal universities, and to all learned societies known to the Institution, as well as to representative men of science in every nation. Suggestions and recommendations in regard to the most effective application of this fund are invited. It is probable that special grants of money may be made to specialists engaged in original investigation upon atmospheric air and its properties. Applications for grants of this nature should have the indorsement of some recognised academy of sciences, or other institution of learning, and should be accompanied by evidences of the capacity of the applicant, in the form of at least one memoir already published by him, based upon original investigation. To prevent misapprehension of the founder's wishes, it is repeated that the discoveries or applications proper to be brought to the consideration of the Committee of Award, may be in the field of any science or any art without restriction, provided only that they have to do with "the nature and properties of atmospheric air in connection with the welfare of man." Information of any kind desired by persons intending to become competitors will be furnished on application. All communications in regard to the Hodgkins Fund, the Hodgkins Prizes, the Hodgkins Medal, and the Hodgkins Fund Publications, or applications for grants of money, should be addressed to S. P. Langley, Secretary of the Smithsonian Institution, Washington, U.S.A.—S. P. LANGLEY, Secretary of the Smithsonian Institution, Washington, March 31, 1893.

MEETINGS FOR THE WEEK.

- MONDAY, May 1st.**—Medical, 8.30. (Annual Oration).
 --- Society of Arts, 8. "Some Masters of Ornament," by Lewis Foreman Day. (Cantor Lectures).
 --- Society of Chemical Industry, 8. "The Gasification of Coal and of Liquid Hydrocarbons," by Dr. P. Dvorkovitch. "Estimation of Tannic and Gallic Acids," by W. P. Dreaper.
 --- Royal Institution, 5. (Annual Meeting).
- TUESDAY, 2nd.**—Institute of Civil Engineers, 8.
 --- Pathological, 8.30.
 --- Royal Institution, 3. "Modern Society in China," by Prof. R. K. Douglas.
 --- Society of Arts, 8. "Russian Industrial Art," by E. Delmar Morgan.
- WEDNESDAY, 3rd.**—Society of Arts, 8. "Practical Electrical Problems at Chicago," by Prof. Silvanus P. Thompson, F.R.S.
- THURSDAY, 4th.**—Royal, 4.30.
 --- Royal Society Club, 6.30.
 --- Royal Institution, 3. "The Atmosphere," by Prof. Dewar, F.R.S.
 --- Chemical, 8. Ballot for the Election of Fellows. "Hydrates of Potassium, Sodium, and Lithium Hydroxides," by S. U. Pickering, F.R.S. "Notes on Marsh's and Reinsch's Tests for Arsenic," by J. Clark, Ph.D. "The Formation of Hydrogen Peroxide in Organic Liquids," by A. Richardson, Ph.D. "The Supposed Saponification of Linseed Oil by White-lead," by J. B. Hannay and A. E. Leighton. "Notes on the Capillary Separation of Substances in Solution," by L. Reed.
- FRIDAY, 5th.**—Royal Institution, 9. "Fogs, Clouds, and Lightning," by Shelford Bidwell, F.R.S.
 --- Geologists' Association, 8.
 --- Quekett Club, 8.
 --- Chemical Society, 8. Hoffman Memorial Meeting. Addresses by the Right Hon. Lord Playfair, Sir F. A. Abel, F.R.S., and W.H. Perkin, F.R.S.
- SATURDAY, 6th.**—Royal Institution, 3. "Johnson and Milton," by Henry Craik, LL.D.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1745.

ON THE ABSORPTION-SPECTRA OF SOME COMPOUNDS OF CHROMIUM.*

By W. LAPRAIK, Ph.D., F.I.C.

In the following research the optical properties of a series of chromium salts have been investigated, which, in part, are recorded for the first time. I referred to the literature on the subject, but more particularly to that relating to chromium oxalate. The main objects of this research were as follows:—

1. To show the spectroscopic relation existing between the complex salts of oxalic acid and chromium, and other metals chemically related to chromium.

2. To determine if similar salts were produced with acids chemically homologous with oxalic acid, and if such existed to determine their spectroscopic relations.

3. To determine if any spectroscopic relation existed between the compounds formed when chromium hydroxide was dissolved in various organic acids, and the known chemical composition of such acids.

Apparatus and Method Employed.

For the examination of the absorption-spectra of the compounds mentioned in this research, I used a single prism spectroscope constructed by Browning. The prism was of extra dense flint-glass, having a refractive surface of 10.9 square c.m. The collimator and telescope lenses were 30 m.m. in diameter. The length of focus of collimator and telescope being 33 c.m., while the magnification of the telescope was 10 diameters. The circle was divided into thirds of a degree, and the vernier was divided into 20 divisions, thus enabling one to read easily to minutes. All readings were made with the assistance of a lens. The slit was fitted with a right angled prism so that two spectra could be superposed. In some experiments—mentioned in the text—two prisms were used, but the dispersion was then too great, with the result that the faint absorption-bands were all but invisible; also in other cases a very fine ruled grating was substituted with a like result.

The Light Source.

It is important in work of this character to have a source of light as constant as possible, and at the same time of sufficient illuminating power. With this idea in view a quick-combustion petroleum-lamp, having a circular wick, was used. This gave a very powerful white light, having an illuminating power of 48 candles (English). In some cases the electric light, and also sun light reflected from a heliostat, were used, but the absorption-spectra given did not differ in any material way from those given by the foregoing arrangement.

The containing vessels for the solutions under examination were similar to those described by Hansen.† They were plate glass troughs, each consisting of two faces, which were perfectly parallel, and another centre-piece, also of plate glass, hollowed out. The three parts were held together by a cement formed by a hot aqueous solu-

tion of isinglass. These troughs had a capacity of 3 to 5 c.c. When a slightly increased thickness in the layer of the solution was required, two or more troughs could be placed one in front of the other, and held together by an indiarubber band. When greater thicknesses were required, as 15 c.m., then glass tubes were used, having their ends ground and fitted with glass plates.

The Determination of Wave-Lengths for the Different Parts of the Scale.

This was accomplished by means of graphical interpolation (Wiedemann-Ebert, *Practicum*, p. 295). The numbers in the following table were observed; under λ are the wave-lengths, and under a are angular measurements from the scale.

	λ .	a .
K α	770.0	34° 25'
	720.0	34° 36'
B	686.7	34° 46'
Lia	670.5	34° 52'
	662.5	34° 56'
C	656.2	34° 58'
D	589.2	35° 30'
	558.0	35° 50'
	531.5	36° 9'
E	526.9	36° 14'
	491.5	36° 45'
F	486.0	36° 53'
	477.0	37° 5'
Sr	361.0	37° 27'
	447.5	37° 48'
	435.0	38° 11'
G	430.7	38° 16'
	425.0	38° 29'
	415.5	38° 46'
K β	404.0	39° 12'
H	396.8	39° 27'

The results are tabulated in an accompanying table.* The measurements are in wave-lengths. Continuous absorption is shown in the first and last columns, and the absorption-bands in the columns numbered 1, 2, 3, 4, 5. Each spectra given is numbered at the side, and when referred to in the text the number of the spectrum is placed in parentheses. Two numbers separated by a short vertical line (e.g., spectrum 4) indicate two separate absorption-bands.

Experiments and Resulting Observations.

Potassium Chromoxalate, $K_2Cr_2O_4 + 6H_2O$ (1 and 2)
—This salt was obtained by the method first proposed by Gregory and modified by Croft, viz., by the action of 19 parts of potassium dichromate on a mixture of a saturated hot solution of 23 parts of potassium oxalate and 55 parts of crystallised oxalic acid; when the action had ceased the solution was evaporated to dryness, re-dissolved in water, and crystallised in a flat-bottomed dish, to which the crystals firmly adhered, and thus could be easily examined by transmitted light. It was found that in some cases the crystals were laid down on different axes, so that some appeared red while others were of the well-known corn-flower blue colour. That the crystals were homogeneous was easily seen on re-solution and re-crystallisation, when no red crystals, but blue ones, were obtained; and, further, on rotating the red-coloured crystals they transmitted blue rays, for they are doubly refractive. The blue light transmitted by the crystals (1) gave continuous absorption to 800; then a thin faint band at 717, then a very dark and sharp band 710—704. Accompanying this are two fainter bands, the centres of which are 683 and 663 respectively; then a broad absorption from 660—518, and lastly continuous absorption from 434. The red light transmitted by the other axes of the crystal could not be so easily examined; the thin, dark,

* In the original memoir there is given a map of the absorption-spectra.

* *Journ. für Prakt. Chemie*, xlvii, 305 (1893).

† *Fahresb.*, vii., 392, (1854); Brewster, *Phil. Mag.*, vi., 305 (1835); Brewster, *Phil. Mag.*, vii., 436 (1835); W. Haidinger, "Ueber den Pleochroismus des oxalsauren Chromoxydkalis," *Pogg. Ann.*, lxxvi., 107 (1849); J. Müller, "Ueber die natürlichen Farbensichtiger Körper," *Pogg. Ann.*, lxxix., 347 (1850); Grailich, "Krystallographische optische Untersuchungen," *Wien*, 146 (1858); Th. Etihad, "Untersuchungen über die Absorption des Lichtes in einigen Chromsalzen," Inaug.-Dissertat., Leipzig, 1875; E. Wiedemann, *Wied. Ann.*, v., 515 (1878); Croft, "Ueber ein neues Oxalat des Kaliumchromats," *Phil. Mag.*, xxi., 197 (1842).

‡ Hansen, "Die Farbstoffe des Chlorophylls." Darmstadt, 1889.

sharp band was seen, but its position could not be measured; but the broad absorption was continuous from 650, the whole of the green and blue of the spectrum being absorbed.

A saturated solution of the salt was now examined. The absorption-spectrum was similar in kind to that given by the blue crystal, all the bands in the one being represented in the other; but their positions in the spectrum are not identical, the bands in the aqueous solution being moved slightly nearer the blue end of the spectrum. The measurements are continuous absorption to 820; a faint band at 710, a strong sharp band at 704—698, a faint band at 681, another faint band at 663; then broad absorption from 642 to 508, and continuous absorption from 474. It will thus be seen that all the bands in the solution are slightly nearer the blue end of the spectrum, excepting in the case of 663, which is faint and difficult to measure.

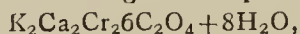
Other Chromoxalates.

It was thought expedient to prepare some other salts analogous to the above, in which the potassium is wholly or in part replaced by other metals, and to determine how their absorption-spectra differed.

Silver Chromoxalate, $\text{Ag}_6\text{Cr}_26\text{C}_2\text{O}_4 + \text{Aq.}$ —This salt is easily made by decomposing the corresponding potassium salt with an equivalent of silver nitrate. The silver salt easily separates by spontaneous evaporation in minute highly coloured crystals. These were, however, too small and opaque to see through, so that their absorption-spectrum could not be examined. An aqueous solution of the salt was made, and this gave an absorption-spectrum identical with that given by the corresponding potassium salt.

Barium Chromoxalate, $\text{Ba}_3\text{Cr}_26\text{C}_2\text{O}_4 + \text{Aq.}$ —This salt is not very soluble in cold water, but by using a considerable thickness of a hot solution, the absorption-spectrum was again found to be the same as that given by the potassium salt.

Now a compound having the composition—



which had been prepared and described by Hartley (*Proc. Roy. Soc.*, xxi., 499) was used. I prepared a hot concentrated solution of this body, and I found as in the previous cases no difference in the absorption-spectrum of this salt and that of the corresponding compound of potassium chromoxalate.

It was now thought to be of some interest to prepare if possible a salt in which part of the potassium in potassium chromoxalate was replaced by ammonium,



For this purpose a hot saturated solution containing 29.5 grms. of potassium dichromate was added to one containing 28.4 grms. crystallised ammonium oxalate and 88.2 grms. crystallised oxalic acid.* After the action had ceased the solution was evaporated to small bulk, and it was then observed that free ammonia escaped with the steam. After standing, a crop of beautifully formed prismatic crystals was obtained which were not distinguishable in appearance from potassium chromoxalate, only that the crystals are usually smaller in size. They also exhibit the well-known corn-flower blue colour when examined by transmitted light. The salt was now subjected to analysis. The analysis of this and analogous salts is surrounded with unusual difficulties.

The ammonia was determined by heating a known weight with a solution of caustic potash and passing the evolved ammonia into standard acid. For the determination of chromium the salt was first carefully decomposed by heat, and then the residue was fused with about three parts its weight of a mixture of sodium carbonate and potassium nitrate. After fusion the mass was dis-

solved in water and acidified with hydrochloric acid, reduced by sulphurous acid, and then precipitated by ammonia solution. The precipitated chromium hydroxide was washed and re-dissolved in hydrochloric acid, and then re-precipitated. This was repeated in all cases at least twice. In some cases the estimation of the chromium was attempted by precipitation as mercurous chromate, using for this purpose mercurous nitrate, while the solution had been previously acidulated by nitric acid, but the alkaline chromate frequently became reduced, and consequently the results were unreliable, and they were therefore discarded. The potassium was estimated as chloride.

The following are the numbers obtained:—

Grm.	Grm.	Per cent.
0.9567 lost at 100°	0.0947	= 9.89 H ₂ O.
0.5819 "	0.0577	= 9.91 H ₂ O.
0.8992 gave "	0.0510 NH ₃	= 6.00 NH ₄ .
0.5819 "	0.1420 KCl	= 12.77 K.
1.6010 "	0.2750 Cr ₂ O ₃	= 11.78 Cr.
1.1935 "	0.2042 Cr ₂ O ₃	= 11.74 Cr.
0.7304 "	0.1240 Cr ₂ O ₃	= 11.55 Cr.

$\text{K}_3(\text{NH}_4)_3\text{Cr}_26\text{C}_2\text{O}_4 + 5\text{H}_2\text{O}.$			Found.		
Calculated.					
H ₂ O	10.07		9.89	9.91	—
NH ₄	6.04		6.00	—	—
K	13.10		12.77	—	—
Cr	11.69		11.78	11.74	11.55

The spectrum of the light transmitted by the crystals of this salt was examined, and again it was found to be identical with the absorption-spectrum given by the crystals of potassium chromoxalate. The salt is easily soluble in water, and it was found that the absorption-spectrum given by this solution was also exactly the same as that given by a solution of potassium chromoxalate. It follows, therefore, that there exist the same relation between the absorption-spectra given by the crystal and by the aqueous solution of both of these salts; that is, that the more important absorption-bands in the case of the crystal are nearer the red end of the spectrum than is the case when either salt is dissolved in water. From the fact* that all these salts give identical spectra when examined under similar conditions, that these bodies do not behave chemically as simple oxalates, and that the potassium of potassium chromoxalate can be replaced either wholly or in part by other metals, it is clear that we are dealing with very stable combinations, such combination, however, being not of the ordinary character of double salts, but more nearly approaching in character bodies like the double cyanides, as, for example, potassium ferricyanide, $\text{K}_6\text{Fe}_2(\text{CN})_{12}$. If such be the case, the chromium in such salts would play the part of part of the acid radicle; and as the acid $\text{H}_6\text{Fe}_2(\text{CN})_{12}$ exists, it does not seem improbable but that a body of the composition $\text{H}_6\text{Cr}_26\text{C}_2\text{O}_4$ may also exist. The first step in this direction was to prepare chromium oxalate and to study its properties.

Chromium Oxalate (3 and 4).

It is well known that chromium hydroxide is soluble in oxalic acid, but there is great difficulty in isolating the oxalate itself.† Graham says ("Graham's Researches," p. 376):—"I made several attempts to crystallise chromium oxalate but without result, so I had no opportunity of studying its constitution in relation to the above" (i.e., potassium chromoxalate).

Two experiments were made. In the first, 113.4 grms. re-crystallised oxalic acid were dissolved in hot water, and to this was added 20 grms. of chromium trioxide (free from sulphuric acid), dissolved in water,—these propor-

* These quantities are those required for the compound—
 $\text{K}_2(\text{NH}_4)_4\text{Cr}_26\text{C}_2\text{O}_4.$

* See also B. O. Peirce and E. Wiedemann, *Wied. Ann.*, v., 515 (1878).
† See also Kistiakowsky, *Zeit. f. Phys. Chem.*, vi., 97 (1890).

tions being those indicated by theory for the preparation of the compound $H_6Cr_2O_4$. After effervescence had ceased, the solution was evaporated to small bulk; in the meantime it changed colour, but finally became light blue by daylight but purple by lamplight. It was put aside to crystallise over sulphuric acid; oxalic acid separated, which was removed from time to time until a thick treacle-like mass remained, which was finally obtained in a semi-crystalline state, and having a dark red colour.

In the second experiment proportionately less oxalic acid was used. The quantities taken were 132 grms. re-crystallised oxalic acid and 30 grms. chromium trioxide (free from sulphuric acid); they were dissolved in water, and treated in the same manner as in the last experiment. The final colour of the solution was also the same. The slight excess of oxalic acid readily crystallised out, and it was removed leaving a thick treacle-like mass as in the last experiment, which finally crystallised. The salt was analysed with the following result:—

Grm.	Grm.	Per cent.	
1.0173 lost at 120°	0.2310	= 22.61	H ₂ O.
0.9484 „ „	0.2130	= 22.46	H ₂ O.
0.3992 gave „	0.1265	= 31.69	Cr ₂ O ₃ .
0.7615 „ „	0.3510	= 46.09	C ₂ O ₃ .
0.8520 „ „	0.3700	= 45.95	C ₂ O ₃ .
Cr ₂ 3C ₂ O ₄ + 6H ₂ O. Calculated.		Found.	
Cr ₂ O ₃	31.99	31.69	—
C ₂ O ₃	45.34	45.95	46.09
H ₂ O	22.67	22.61	22.46

The C₂O₃ was determined by Graham's method, viz., by heating the salt with concentrated sulphuric acid and noting the loss due to CO₂ and CO.

The salt, hydrated chromium oxalate, when seen in mass is nearly black, but in thin layers it is reddish-blue. It is very soluble in water, the solution being reddish-blue by lamplight. It is deliquescent. It is soluble in ordinary alcohol, but the anhydrous salt does not appear to be soluble in dry alcohol. The anhydrous salt is obtained by heating the hydrated salt to 120° C.; it has a fine deep green colour. Curiously enough it does not appear to be immediately soluble in cold water; after standing some time, however, it becomes hydrated and then dissolves. In hot water it is instantly soluble. It gives no precipitate with calcium chloride or with silver nitrate solutions, as complex salts are thus formed. Sodium carbonate solution does not yield a precipitate in the cold, but the solution becomes green, and on boiling is precipitated. Potassium bicarbonate both in solution and in the solid state produces a vigorous effervescence. A very thin layer of a saturated solution of the salt dissolved in water gave the following absorption spectrum (3).

Continuous absorption ending about 714. Then a rather broad, somewhat indefinite band from 704—689. Then a shadow at 653 joining the broad absorption from 610—503. Then some blue light transmitted, and finally continuous absorption from 471.

It is to be observed that the absorption-spectrum of a solution of chromium oxalate is not the same as that given by the chromoxalates under the same conditions. The dominant band is much broader and less distinct in the case of chromium oxalate; its edges are blunter, and gradually merge into the lighter part of the spectrum. They both begin at the same point, 704, but in no other respect do they resemble one another. Altering the thickness of the layer of solution under examination does not bring out any further similarity, and lastly, the three fainter bands in the chromoxalates are entirely absent in chromium oxalate. The absorption-spectrum of the chromoxalates then is not that of chromium oxalate; in other words, the absorption-spectrum of the chromoxalates is not entirely due to the vibrations of *part* of the molecule, but to the vibrations of the whole combina-

tion; and as far as these experiments go, it seems that the more positive part of the combination has no influence in damping the molecular vibrations.

A solution of chromium oxalate was made by digesting an *excess* of chromium hydroxide in a concentrated aqueous solution of oxalic acid. The filtered solution gave exactly the same spectrum as the foregoing. The same remark applies to the absorption-spectrum given by the alcoholic solution of hydrated chromium oxalate.

The solid chromium oxalate is somewhat difficult to examine for its absorption spectrum, but by evaporation of a solution of the salt on a glass slide I was able to see that the dominant band appeared to be slightly nearer the red end of the spectrum than was the case in the solution. Although no compound of chromium oxalate and oxalic acid crystallises on evaporation of a solution containing these substances, yet there is reason for believing that there are two such compounds which exist in solution.

It was observed that if chromium oxalate be dissolved in water, and then some oxalic acid added, and if the solution be gently warmed, an absorption-spectrum is obtained giving two sharp, dark, thin bands in the red part of the spectrum, and the three fainter incidental bands as well, which is so characteristic of the chromoxalates, but which are not given by chromium oxalate itself. The significance of this two-lined spectrum will be again referred to under the red potassium chromoxalate. The absorption-spectrum (4) is as follows.

Continuous absorption ending about 800. Then a faint band at 710. A sharp, thin, very dark band, the centre of which is 704. A somewhat fainter but equally sharp band, its centre being 695. Then the two other incidental bands at 681 and 663, respectively. The broad absorption at 650—505, and continuous absorption from 471.

By prolonged heating of this solution, and if necessary a further addition of oxalic acid, the band at 695 fades out, and finally disappears altogether, and there remains an absorption-spectrum agreeing in all particulars with that given by the chromoxalates, and that in a solution originally containing only chromium oxalate and oxalic acid.

It has been shown that the chromoxalates of the metals give identical absorption-spectra; one should, therefore, expect that the compound hydrogen chromoxalate would also give the same absorption-spectrum. Therefore, I think one is forced to the conclusion that it is this compound, hydrogen chromoxalate, which gives an absorption-spectrum agreeing in all points with that given by other chromoxalates. Although I have not succeeded in isolating this body yet, there are strong reasons given above for believing in its existence.

(To be continued).

THE CHEMICAL CONSTITUTION OF THE ATMOSPHERE, AND ITS BEARING ON GEOLOGICAL CHANGES.

By JAMES MORRIS.

IN the CHEMICAL NEWS, vol. lxvii., p. 135, there is an article by Dr. Phipson, in which he expressed some of his own views, and also partly quotes those of the late Prof. Koene. At p. 309 of the preceding volume I described my experiments on the mineralisation of alumina, carbonic acid being the agent used. I spoke of the experiments of Sir James Hall, and more particularly of Doelter's modification of these experiments. The latter mineralogist found that when a plentiful supply of carbonic acid was present, the mineralisation occurred without pressure. This latter factor in geological change may in some cases have been overrated, and perhaps such considerations

have tended to retard attempts at the synthesis of minerals.

In considering the factor of pressure in geology, a distinction must be made between the constant pressure caused by superincumbent mass, and the variable, and in some cases temporary, pressure caused by expansion and contraction. Minerals deep down in the earth are sometimes mechanically protected from pressure of the former kind. In any case the results of Doelter's experiments are noteworthy.

From the presence of combustible substances in the primitive rocks, from the enormous leaves of the plants which formed the coal-flora, from beings capable of existing without free oxygen, and from the higher excitability of modern man, the general opinion expressed in Dr. Phipson's article is that the amount of carbonic acid in the atmosphere has gradually diminished, and that of free oxygen increased.

In most cases the available evidence in the inorganic world is more direct and measurable than that in the organic. In certain phases of geological evidence, however, the case is reversed. Thus, the petrified remains of a tree, or of a crab, give us a veritable stone picture of the plant or animal, often with great perfection of detail. What various metamorphoses many minerals may have undergone is neither measurable nor imaginable.

Koene's doctrine, the starting-point of which is that the atmosphere in earlier geological ages consisted of nitrogen, carbonic acid, and vapour of water, may yet come to receive some confirmation from the still somewhat neglected science of mineral synthesis.

Regard must be had to the temperature of dissociation of the carbonic acid and the water vapour, compared with that of the solidification of the earth's crust. Perhaps we may at least assume that many mineralogical transformations took place during the cooling of the crust at a period when the atmosphere still contained a large proportion of carbonic acid. The enormous quantity of this gas still evolved in volcanic regions is perhaps the residue of a vastly greater proportion present in earlier times. The presence of carbonic acid and carbonic oxide in meteorites should not be overlooked.

The remarks already made may suggest some thoughts in regard to the interdependence of the sciences.

217, West George Street, Glasgow,
April, 1893.

MAGNETIC PROPERTIES OF LIQUID OXYGEN.*

By Prof. DEWAR, M.A., LL.D., F.R.S.

AFTER alluding to the generous aid which he had received both from the Royal Institution and from others in connection with his researches on the properties of liquid oxygen, and to the untiring assistance rendered him by his co-workers in the laboratory, Prof. Dewar said that on the occasion of the commemoration of the centenary of the birth of Michael Faraday he had demonstrated some of the properties of liquid oxygen. He hoped that evening to go several steps further, and to show liquid air, and to render visible some of its more extraordinary properties.

The apparatus employed consisted of the gas-engine downstairs, which was driving two compressors. The chamber containing the oxygen to be liquefied was surrounded by two circuits, one traversed by ethylene, the other by nitrous oxide. Some liquid ethylene was admitted to the chamber belonging to its circuit, and there evaporated. It was then returned to the compressor as gas, and liquefied, and thence again into the chamber as required. A similar cycle of operations was carried out with the nitrous oxide. There was a hundredweight

of liquid ethylene prepared for the experiment. Ethylene was obtained from alcohol by the action of strong sulphuric acid. Its manufacture was exceedingly difficult, because dangerous, and as the efficiency of the process only amounted to 15 or 20 per cent, the preparation of a hundredweight of liquid was no light task. The cycle of operations, which for want of time was not fully explained, was the same as that commonly employed in refrigerating machinery working with ether or ammonia.

The lecturer then exhibited to the audience a pint of liquid oxygen, which by its cloudy appearance showed that it contained traces of impurity. The oxygen was filtered, and then appeared as a clear transparent liquid with a slightly blue tinge. The density of oxygen gas at -182°C . is normal, and the latent heat of volatilisation of the liquid is about 80 units. The capillarity of liquid oxygen at its boiling-point was about one-sixth that of water. The temperature of liquid oxygen at atmospheric pressure, determined by the specific heat method, using platinum and silver, was -180°C .

Reference was then made to a remarkable experimental corroboration of the correctness for exceedingly low temperatures of Lord Kelvin and Prof. Tait's thermo-electric diagram. If the lines of copper and platinum were prolonged in the direction of negative temperature, they would intersect at -95°C . Similarly, the copper and palladium lines would cut one another at -170°C . Now if this diagram were correct, the E.M.F. of the thermo-electric junctions of these two pairs of metals should reverse at these points. A Cu-Pt junction connected to a reflecting galvanometer was then placed in oxygen vapour and cooled down. At -100°C . the spot of light stopped and reversed. A Cu-Pd junction was afterwards placed in a tube containing liquid oxygen, and a similar reversal took place at about -170°C .

Liquid oxygen is a non-conductor of electricity; a spark, taken from an induction coil one m.m. long, in the liquid requires a potential equal to a striking distance in air of 25 m.m. It gave a flash now and then, when a bubble of the oxygen vapour in the boiling liquid came between the terminals. Thus liquid oxygen is a high insulator. When the spark is taken from a Wimshurst machine the oxygen appears to allow the passage of a discharge to take place with much greater ease. The spectrum of the spark taken in the liquid is a continuous one, showing all the absorption-bands.

As to its absorption-spectrum, the lines A and B of the solar spectrum are due to oxygen, and they came out strongly when the liquid was interposed in the path of the rays from the electric lamp. Both the liquid and the highly compressed gas show a series of five absorption-bands, situated respectively in the orange, yellow, green, and blue of the spectrum.

Experiments prove that gaseous and liquid oxygen have substantially the same absorption-spectrum. This is a very noteworthy conclusion considering that no compound of oxygen, so far as is known, gives the absorptions of oxygen. The persistency of the absorption through the stages of gaseous condensation towards complete liquidity, implies a persistency of molecular constitution which we should hardly have expected. The absorptions of the class to which A and B belong must be those most easily assumed by the diatomic molecules (O_2) of ordinary oxygen; whereas the diffuse bands above referred to, seeing they have intensities proportional to the square of the density of the gas, must depend on a change produced by compression. This may be brought about in two ways, either by the formation of more complex molecules, or by the constraint to which the molecules are subjected during their encounters with one another.

When the evaporation of liquid oxygen is accelerated by the action of a high expansion-pump and an open test-tube is inserted into it, the tube begins to fill up with liquid atmospheric air, produced at the ordinary barometric pressure.

* Abstract of a Lecture delivered at the Royal Institution of Great Britain, Friday, June 10, 1892.

Dr. Janssen had recently been making prolonged and careful experiments on Mont Blanc, and he found that these oxygen lines disappeared more and more from the solar spectrum as he reached higher altitudes. The lines at all elevations come out more strongly when the sun is low, because the rays then have to traverse greater thicknesses of the earth's atmosphere.

Michael Faraday's experiments made in 1849 on the action of magnetism on gases opened up a new field of investigation. The following table, in which + means "magnetic" and - means "negative," summarises the results of Faraday's experiments.

Magnetic Relations of Gases (Faraday).

	In air.	In car- bonic acid.	In hydrogen.	In coal- gas.
Air	o	+	+weak	+
Nitrogen	-	-	-strong	-
Oxygen	+	+	+strong	+strong
Carbonic acid . .	-	o	-	-weak
Carbonic oxide . .	-	-	-	-weak
Nitric oxide . . .	-weak	+	+	..
Ethylene	-	-	-	+weak
Ammonia	-	-	-	..
Hydrochloric acid	-	-	-weak	..

Becquerel was before Faraday in experimenting upon this subject. Becquerel allowed charcoal to absorb gases, and then examined the properties of such charcoal in the magnetic field. He thus discovered the magnetic properties of oxygen to be strong, even in relation to a solution of ferrous chloride, as set forth in the following table:—

Specific Magnetism, Equal Weights (Becquerel).

Iron	+1,000,000
Oxygen	+ 377
Ferrous chloride solution, sp. gr. 1.4334	+ 140
Air	+ 88
Water	- 3

The lecturer took a cup made of rock salt, and put in it some liquid oxygen. The liquid did not wet rock salt, but remained in a spheroidal state. The cup and its contents were placed between and a little below the poles of an electro-magnet. Whenever the circuit was completed, the liquid oxygen rose from the cup and connected the two poles. Then it boiled away, sometimes more on one pole than the other, and when the circuit was broken it fell off the pole in drops back into the cup. He also showed that the magnet would draw up liquid oxygen out of a tube. A test tube containing liquid oxygen when placed in the Hughes balance produced no disturbing effect. The magnetic moment of liquid oxygen is about 1000 when the magnetic moment of iron is taken as 1,000,000. On cooling, some bodies increased in magnetic power. Cotton-wool, moistened with liquid oxygen, was strongly attracted by the magnet, and the liquid oxygen was actually sucked out of it on to the poles. A crystal of ferrous sulphate, similarly cooled, stuck to one of the poles.

The lecturer remarked that fluorine is so much like oxygen in its properties, that he ventured to predict that it will turn out to be a magnetic gas.

Nitrogen liquefies at a lower temperature than oxygen, and one would expect the oxygen to come down before the nitrogen when air is liquefied, as stated in some textbooks, but unfortunately it is not true. They liquefy together. In evaporating, however, the nitrogen boils off before the oxygen. He poured two or three ounces of liquid air into a large test-tube, and a smouldering splinter of wood dipped into the mouth of the tube was not ignited; the bulk of the nitrogen was nearly five minutes in boiling off, after which a smouldering splinter dipped into the mouth of the test-tube burst into flame.

Between the poles of the magnet all the liquefied air went to the poles; there was no separation of the oxygen

and nitrogen. Liquid air has the same high insulating power as liquid oxygen. The phenomena presented by liquefied gases present an unlimited field for investigation. At -200°C . the molecules of oxygen had only one-half of their ordinary velocity, and had lost three-fourths of their energy. At such low temperatures they seemed to be drawing near what might be called "the death of matter," so far as chemical action was concerned; liquid oxygen, for instance, had no action upon a piece of phosphorus and potassium or sodium dropped into it; and once he thought and publicly stated, that at such temperatures all chemical action ceased. That statement required some qualification, because a photographic plate placed in liquid oxygen could be acted upon by radiant energy, and at a temperature of -200°C . was still sensitive to light.

Prof. M'Kendrick had tried the effect of these low temperatures upon the spores of microbic organisms, by submitting in sealed glass tubes blood, milk, flesh, and such-like substances, for one hour to a temperature of -182°C ., and subsequently keeping them at blood heat for some days. The tubes on being opened were all putrid. Seeds also withstood the action of a similar amount of cold. He thought, therefore, that this experiment had proved the possibility of Lord Kelvin's suggestion, that life might have been brought to the newly-cooled earth upon a seed-bearing meteorite.

In concluding, the lecturer heartily thanked his two assistants, Mr. R. N. Lennox and Mr. J. W. Heath, for the arduous work they had had in preparing such elaborate demonstrations.

ON THE DENSITIES OF THE PRINCIPAL GASES.*

By Lord RAYLEIGH, Sec. R.S.

(Concluded from p. 200).

Reduction to Standard Pressure.

THE pressure to which the numbers so far given relate is that due to 762.511 m.m. of mercury at a temperature of 14.85°F , and under the gravity operative in my laboratory in latitude $51^{\circ}47'$. In order to compare the results with those of other experimenters, it will be convenient to reduce them not only to 760 m.m. of mercury pressure at 0° , but also to the value of gravity at Paris. The corrective factor for length is $760/762.511$. In order to correct for temperature we will employ the formula (Everett, p. 142) $1 + 0.0001818 t + 0.0000000017 t^2$ for the volume of mercury at t° . The factor of correction for temperature is thus 1.002700. For gravity we may employ the formula—

$$g = 980.6056 - 2.5028 \cos 2\lambda,$$

λ being the latitude. Thus, for my laboratory—

$$g = 981.193,$$

and for Paris—

$$g = 980.939,$$

the difference of elevation being negligible. The factor of correction is thus 0.99974.

The product of the three factors, corrective for length, for temperature, and for gravity, is accordingly 0.99914. Thus multiplied, the numbers are as follows:—

Air.	Oxygen.	Nitrogen.
2.37512	2.62534	2.30883

and these may now be compared with the water contents of the globe, viz., 1836.52.

The densities of the various gases under standard conditions, referred to that of distilled water at 4° , are thus:—

* A Paper read before the Royal Society.

† The thermometer employed with the manometer read 0.15° too high.

Air.	Oxygen.	Nitrogen.
0.00129327	0.00142952	0.00125718

With regard to hydrogen, we may calculate its density by means of the ratio of densities of oxygen and hydrogen formerly given by me, viz., 15.882. Hence—

Hydrogen 0.000090009.

The following Table shows the results arrived at by various experimenters. Von Jolly did not examine hydrogen. The numbers are multiplied by 1000 so as to exhibit the weights in grms. per litre:—

	Air.	Oxygen.	Nitrogen.	Hydrogen.
Regnault, 1847 ..	1.29319	1.42980	1.25617	0.08958
Corrected by Crafts	1.29349	1.43011	1.25647	0.08988
Von Jolly, 1880 ..	1.29351	1.42939	1.25787	—
Ditto corrected ..	1.29383	1.42971	1.25819	—
Leduc, 1891* ..	1.29330	1.42910	1.25709	0.08985
Rayleigh, 1893 ..	1.29327	1.42952	1.25718	0.09001

The correction of Regnault by Crafts (*Comptes Rendus*, cvi., p. 1664) represents allowance for the contraction of Regnault's globe when exhausted, but the data were not obtained from the identical globe used by Regnault. In the fourth row I have introduced a similar correction to the results of von Jolly. This is merely an estimate founded upon the probability that the proportional contraction would be about the same as in my own case and in that of M. Leduc.

In taking a mean we may omit the uncorrected numbers, and also that obtained by Regnault for nitrogen, as there is reason to suppose that his gas was contaminated with hydrogen. Thus—

	Air.	Oxygen.	Nitrogen.	Hydrogen.
Mean numbers ..	1.29347	1.42961	1.25749	0.08991

The evaluation of the densities as compared with water is exposed to many sources of error which do not affect the comparison of one gas with another. It may therefore be instructive to exhibit the results of various workers referred to air as unity.

	Oxygen.	Nitrogen.	Hydrogen.
Regnault (corrected) ..	1.10562	0.97138	0.06949
Von Jolly (corrected) ..	1.10502	0.97245	—
Leduc	1.1050	0.9720	0.06947
Rayleigh	1.10535	0.97209	0.06960
Mean	1.10525	0.97218	0.06952

As usually happens in such cases, the concordance of the numbers obtained by various experimenters is not so good as might be expected from the work of each taken separately. The most serious discrepancy is in the difficult case of hydrogen. M. Leduc suggests (*Comptes Rendus*, July, 1892) that my number is too high on account of penetration of air through the blow-off tube (used to establish equilibrium of pressure with the atmosphere), which he reckons at 1 m. long and 1 c.m. in diameter. In reality the length was about double, and the diameter one-half of these estimates; and the explanation is difficult to maintain, in view of the fact, recorded in my paper, that a prolongation of the time of contact from 4^m to 30^m had no appreciable ill effect. It must be admitted, however, that there is a certain presumption in favour of a lower number, unless it can be explained as due to an insufficient estimate for the correction for contraction. On account of the doubt as to the appropriate value of this correction, no great weight can be assigned to Regnault's number for hydrogen. If the atomic weight of oxygen be indeed 15.88, and the ratio of densities of oxygen and hydrogen be 15.90, as M. Leduc makes them, we should have to accept a much higher number for the ratio of volumes than that (2.0002) resulting from the very elaborate measurements of Morley. But while I write the information reaches me that Mr. A. Scott's

recent work upon the volume ratio leads him to just such a higher ratio, viz., 2.00245, a number *a priori* more probable than 2.0002. Under the circumstances both the volume ratio and the density of hydrogen must be regarded as still uncertain to the 1-1000th part.

NOTE A.

On the Establishment of Equilibrium of Pressure in Two Vessels Connected by a Constricted Channel.

It may be worth while to give explicitly the theory of this process, supposing that the difference of pressures is small throughout, and that the capacity of the channel may be neglected. If $v_1 p_1$ denote the volume and pressure of the gas in the first vessel at time t , $v_2 p_2$ the corresponding quantities for the second vessel, we have—

$$v_1 dp_1/dt + c(p_1 - p_2) = 0,$$

$$v_2 dp_2/dt + c(p_2 - p_1) = 0,$$

where c is a constant which we may regard as the conductivity of the channel. In these equations inertia is neglected, only resistances of a viscous nature being regarded, as amply suffices for the practical problem. From the above we may at once deduce—

$$\frac{d(p_1 - p_2)}{dt} + \left(\frac{c}{v_1} + \frac{c}{v_2} \right) (p_1 - p_2) = 0;$$

showing that $(p_1 - p_2)$ varies as e^{-qt} , where—

$$q = \frac{c}{v_1} + \frac{c}{v_2} = \frac{1}{\tau},$$

if τ be the time in which the difference of pressures is reduced in the ratio of $e : 1$.

Let us now apply this result (a) to the case where the globe of volume v_1 communicates with the atmosphere, (b) to the case where the globe is connected with a manometer of relatively small volume v_2 . For (a) we have—

$$1/\tau = c/v_1,$$

and for (b)—

$$1/\tau = c/v_2;$$

so that—

$$\tau/\tau' = v_1/v_2.$$

For such a manometer as is described in the text, the ratio v_1/v_2 is at least as high as 30; and in this proportion is diminished the time required for the establishment of equilibrium up to any standard of perfection that may be fixed upon.

THE USE OF ALUM IN BAKING POWDER.

THE case of James James, Appellant, *v.* Evan Jones, Respondent, recently decided at Swansea after five days hearing, presents some points of general interest, as it deals with a subject which had previously been little investigated.

It was an appeal to Quarter Sessions from the Justices' decision inflicting a fine for the sale of baking powder of which alum formed a constituent. Omitting the points which are of legal rather than of scientific interest the case may be stated as follows:—

The powder consisted of about 40 per cent potash alum, 22 per cent bicarbonate of soda, and 38 per cent ground rice.

For the respondent, independent experiments by Prof. Dunstan, Prof. Claude Thompson, and Dr. Otto Hehner showed that hydrate of alumina dried at 212° F. dissolved in hydrochloric acid of 0.2 per cent strength, that strength being taken on the authority of the principal physiological treatises as fairly representing the average strength of the free hydrochloric acid in gastric juice.

Prof. Thompson showed that the result was the same when the temperature of drying was raised to 250° F., and the strength of the acid diminished to 0.04 per cent. It was shown that the temperature of the inside of a loaf during baking did not exceed 212° F.

* *Bulletin des Séances de la Société de Physique.*

Prof. Dunstan, who had fully investigated the matter for the Glamorgan County Council, showed further that the hydrate dried at 212° F. was soluble in the gastric juice of a dog diluted to 0.2 per cent strength, and that the gastric juice of a dog diluted to this extent dissolved hydrate of alumina from bread baked with the powder. That the hydrate of alumina in the bread interfered with the digestion of starch by ptyalin (diastase was used in the actual experiment) and with both peptic and pancreatic digestion. Further, that dilute solution of carbonate of soda of 0.3 per cent strength, the strength of the alkali in intestinal juice, would dissolve hydrate and phosphate of alumina, either freshly precipitated or dried at 212° F., so that absorption of aluminium compounds could occur from the intestine. This was confirmed by his observation that aluminium compounds occurred in the urine of a man who had daily taken 15 to 30 grains of the hydrate dried at 212° F. On one occasion the taking of this quantity of hydrate produced vomiting.

For the appellant, it was contended that the man took much larger quantities of hydrate than would be taken in food, and an attempt was made to draw a distinction between the hydrate as it exists in bread and the hydrate prepared pure and dried at 212° F. No experimental evidence was brought in support of this latter contention.

The experiments with the gastric juice of a dog were objected to on the ground that the gastric juice of carnivora contained a larger proportion of acid than that of man; but, in reply, it was pointed out that the gastric juice of the dog used was diluted to 0.2 per cent—the average strength of human juice.

Mr. W. Morgan, Public Analyst, Swansea, made the following experiment:—He and his son took hydrate of alumina, which had been heated to the temperature of a loaf during baking, either during or after a meal. After about two hours, vomiting was produced by mustard and warm water. The vomit was filtered and the filtrate placed in a dialyser with parchment paper membrane. After leaving all night, aluminium chloride was found to have dialysed. In another experiment, vomiting was produced without taking the hydrate. The vomit was divided into two portions; one was dialysed directly, the other after warming with the hydrate at 105° F. On examination, aluminium chloride was found in the dialysed liquid in the latter case, while none could be found in the blank experiment.

It was contended that these experiments were unfair because the hydrate was used as such, and not in bread. The experiment was repeated for the appellant by Dr. Luff, the Official Analyst to the Home Office, Mr. Sutton, and Dr. Blyth, on one of the witnesses for the appellant during the hearing of the case, with the modification that the man was fed with 1 lb. of bread made with the baking powder, and that the bladder of a recently killed sheep was used as a membrane. It was objected by the respondent that this experiment might be inconclusive, for in view of the use made of aluminium salts in tanning, it could not be expected that aluminium chloride would dialyse through fresh bladder. The bladder was also only washed with cold water, and was therefore presumably not free from mucus. In reply to this the bladder was subsequently tested and found free from aluminium compounds. It was further objected that the man drank $1\frac{1}{2}$ pint of water while eating the bread. This would greatly dilute the gastric juice. The total amount vomited was about 1 pint, so that the quantity of aluminium compound present could not have been large. The dialysed liquid was only tested by adding ammonia after boiling with nitric acid; it was not evaporated and ignited to destroy organic matter.

Dr. Lauder Brunton gave evidence as to the astringent action of aluminium chloride, and generally as to the injurious effects likely to ensue from the absorption of aluminium compounds.

It was contended on behalf of the respondent that these experiments proved that hydrate of alumina was soluble

in the digestive canal, and would produce the same injurious effects as alum; that it would have an irritant and astringent action on the membrane of the stomach, and would interfere with digestion. Further, that absorption of some aluminium compound was proved, and that the introduction into the system of an entirely foreign element could hardly fail to be injurious.

On behalf of the appellant practically no attempt was made to prove that alum itself was not injurious. It was, however, admitted by the respondent that, by the action of the bicarbonate of soda in the powder, it was completely converted into hydrate of alumina; and it was contended by the appellant that this hydrate was insoluble in the digestive canal, and, as an inert substance, passed unchanged through the body; its small amount (6 grains hydrate per pound of bread) would render it perfectly harmless. Further, that if it did dissolve, the small quantity of chloride of aluminium formed would be harmless.

Before the hearing of the case the following experiments had been made in support of the contention that the hydrate was an inert body:—

Mr. Sutton some years ago fed pigs for eight days exclusively with bread made with the baking-powder. They thrived well, and after death alumina was detected in the contents of the intestine, while none could be found in the blood or in the urine contained in the bladder at death. In reply it was contended that the first result proved nothing; with regard to the second the quantity of urine examined was too small for a negative result to prove conclusively that no absorption had taken place. Further, there was no evidence that the pigs were not, as usual, fasted for twenty-four hours before slaughter; if this were done it might materially influence the result.

Dr. Luff prepared hydrate of alumina which was dried at 300° F. Several portions of the "dried hydrate of alumina" were treated with 35 to 40 c.c. each of hydrochloric acid of 0.02 per cent strength, which Dr. Luff stated he believed to be the strength in the gastric juice in the human body.

Eight tubes were warmed to 98.4° F., and one was tested at the end of each hour in the following manner:—On filtering and adding ammonia no precipitate was obtained, even if the filtrate was previously concentrated.

In criticism of these experiments it was contended, first, that the temperature at which the substance was dried greatly exceeded that in the interior of a loaf during baking. The substance was not analysed; there was no proof that it was hydrate of alumina at all, as it might have lost water. Proof of its composition was all the more necessary as a sample of "dried hydrate of alumina" had on a previous day been handed up to the Bench by Mr. Sutton, which had been heated to low redness and was afterwards admitted to be oxide. Secondly, that the strength of the hydrochloric acid used did not fairly represent the strength of the acid in gastric juice, which was generally accepted as about 0.2 per cent instead of 0.02 per cent. When asked for his authority Dr. Luff referred to a Table given in "Halliburton's Chemical Physiology," and stated that recent experiments showed that the strength 0.2 per cent was too high. It was, however, shown by the respondent that the Table in "Halliburton" was taken from the experiments of Schmidt, published in 1855, and that Halliburton, while quoting the results, actually pointed out that the acidity was below the normal, possibly owing to the juice having been obtained from a woman with gastric fistula. Halliburton, like other physiologists, accepted 0.2 per cent as the strength to be used in making artificial gastric juice.

Dr. Luff admitted in cross examination that he had made no notes of these experiments, and stated that it was not his habit to make notes of merely qualitative experiments.

Dr. Richardson stated his opinion that the powder was harmless. He said that he did not consider it proved that aluminium chloride was formed in the stomach, and

that even if aluminium chloride were formed, it could not be absorbed as it coagulates the blood. It was pointed out that it was not contended that aluminium was absorbed as chloride and that chloride of iron was given as a medicine in cases of anæmia. Dr. Richardson said that it was not proved that iron was absorbed in such cases. He declined to make any statement as to the strength of the acid in the gastric juice.

Dr. Winter Blyth expressed his opinion that the baking-powder was not injurious. He brought forward no experiments, except the one already described, performed whilst the case was in progress. He stated that if injury were caused by alum baking-powders it must have become known to medical officers of health.

Many medical men were called and expressed the opinion that the baking-powder was not injurious, stating that they had either used it themselves in their families or had known it used by others without harmful results. Other witnesses also stated that they had used it without harm. It was, however, shown that in most cases the quantity used was very small, much smaller than would be taken by a person feeding largely on bread baked with the powder.

The appeal was dismissed with costs, and the conviction affirmed.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

Annual Meeting, Monday, May 1, 1893.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1892, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Real and Funded Property now amounts to above £104,000, entirely derived from the contributions and donations of the members and of others appreciating the value of the work of the Institution.

Sixty-three new members were elected in 1892.

Sixty-three lectures and twenty evening discourses were delivered in 1892.

The books and pamphlets presented in 1892 amounted to about 238 volumes, making, with 530 volumes (including periodicals bound) purchased by the managers, a total of 768 volumes added to the library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as officers for the ensuing year:—

President—The Duke of Northumberland, K.G., D.C.L., LL.D.

Treasurer—Sir James Crichton-Browne, M.D., LL.D., F.R.S.

Secretary—Sir Frederick Bramwell, Bart., D.C.L., LL.D., F.R.S., M.Inst.C.E.

Managers—Captain W. de W. Abney, C.B., R.E., D.C.L., F.R.S.; Shelford Bidwell, M.A., F.R.S.; John Birkett, F.R.C.S.; Joseph Brown, C.B., Q.C.; Sir Douglas Galton, K.C.B., D.C.L., LL.D., F.R.S.; David Ed. Hughes, F.R.S.; Alfred Bray Kempe, M.A., F.R.S.; George Matthey, F.R.S.; Hugo Müller, Ph.D., F.R.S.; The Right Hon. Earl Percy, F.S.A.; William Chandler Roberts-Austen, C.B., F.R.S.; Sir David Salomons, Bart., M.A., F.R.A.S., F.C.S.; Alexander Siemens, M.Inst.C.E.; Basil Woodd Smith, F.R.A.S., F.S.A.; Sir Richard Webster, M.P., Q.C., LL.D.

Visitors—Charles Edward Beevor, M.D., F.R.C.P.; Henry Arthur Blyth; Francis Woodhouse Braine,

F.R.C.S.; John Tomlinson Brunner, M.P.; Michael Carteighe, F.C.S.; Rookes Evelyn Crompton, M.Inst.C.E.; James Farmer, J.P.; Robert Hannah; Donald William Charles Hood, M.D., F.R.C.P.; Raphael Meldola, F.R.S.; Lachlan Mackintosh Rate, M.A.; Boverton Redwood, F.C.S.; John Callander Ross; John Bell Sedgwick, J.P., F.R.G.S.; George Andrew Spottiswoode.

NOTICES OF BOOKS.

A Dictionary of Applied Chemistry. By T. E. THORPE, B.Sc. (Vict.), Ph.D., D.Sc. (Dublin), F.R.S. Assisted by Eminent Contributors. In Three Volumes. Vol. III. London and New York: Longmans, Green, and Co. 1893. 8vo., 1058 pp.

THIS concluding part of Dr. Thorpe's great work is fully on a level with the two preceding volumes.

Concerning noble opal, we learn that the Hungarian mines of this precious stone still employ two hundred workmen.

The recent extension of the cultivation of opium is a remarkable fact. As far back as 1882 the annual production in the South-West of China was more than twice the whole importation from India. In a few years the use of Indian opium, if it survives at all, will be confined to a few wealthy connoisseurs. Hence it follows that the anti-opium agitation will soon lose its *raison d'être*. It follows also that the alleged anxiety of the Chinese Government to suppress opium-smoking is not *bona fide*.

The section on pigments is exceedingly elaborate, though we find no mention of mineral lake, stannic chromate, a colour closely resembling in tone the lighter madder-lake, but according to Gentele absolutely permanent.

Pure scarlet mercuric iodide, known also as geranium red, is certainly inferior to vermilion in permanence. We have observed, however, that, obtained in the dry way by grinding up mercury with a sufficient proportion of iodine,—the reaction being attended with the development of light and heat,—it is much less fugitive than if prepared in the moist way.

The writer distinguishes carmine from cochineal lakes, as containing a larger proportion of colouring matter and less alumina.

To the dyer and tissue-printer it sounds strange to hear indigo characterised as "very fugitive."

As regards the metallurgy of platinum, the eminent merit of Messrs. Johnson, Matthey, and Co. is fully and justly shown.

The articles on sodium, spectrum analysis, and sulphur may almost be regarded as monographs of their respective subjects.

Under tea we find mention of some very interesting facts. The consumption of tea in Australia amounts to 9 lbs. per head; in China, in Britain, and South Africa, 5 lbs.; in Holland, 0.91 lb.; and in Russia, 0.43 lb. In France, Germany, &c., the consumption of tea is insignificant. It is a remarkable fact mentioned here, though not explained, that Chinese tea keeps better than the produce of India and Ceylon. A fact which should interest the consumer is that in five minutes boiling water extracts practically all the theine, the essential oil, but not more than one-third of the tannin. Robert Fortune is here quoted as including Ireland among the parts of the earth best suited for the cultivation of the tea-plant, whilst in the next sentence we read that a "warm climate is essential, and that in the best districts of China the ordinary range of the thermometer in the summer at 3 p.m. is between 80° and 90°."

A great advantage of Indian tea is its superior cleanliness, as machinery is almost exclusively used in its manufacture. The significance of this point will be appre-

ciated if we remember the intense dirtiness of the Chinese working population.

Under tellurium we are reminded that, according to Brauner, it is probably a mixture of true tellurium with some unknown bodies.

Under tobacco we find it stated—as we believe with full truth—that its growth in Britain, as a field crop, did not in 1886 receive a fair and full trial. The use of kainite and common salt as manures was a complete mistake. Where potash was deficient it should have been supplied in the state of sulphate. It is to be noted that whilst in England the home cultivation of tobacco was suddenly and harshly stopped in 1782, the plantations being destroyed and the planters heavily fined and imprisoned, in Ireland it survived down to 1831.

The article on water is ably and comprehensively written. The notion of “previous sewage contamination” is not accepted. The celebrated “Recommendations” of the Royal Rivers Commission are not quoted, and no unitary method is laid down for dealing with polluted waters. The question as to the relative sanitary value of hard and soft waters is very fairly handled, the conclusion being that the difference of their action upon human health is not well marked. For technical purposes the necessity of pure water is, however, strongly insisted upon.

Under wine we read that vines are very apt to degenerate in a novel district. French vines have not given satisfaction in America, and, on the other hand, American vines transplanted to the Gironde “yielded no potable wine.” These latter experiments are much to be deplored, since they seem to have introduced the phylloxera into Europe. But, on the other hand, European vines do not appear to have degenerated in Australia.

The author's opinion concerning “plastered” wines is decidedly condemnatory. But the attempts at “deplastering” have been decidedly mistaken. They have depended on the use of barium and strontium salts. The salts of barium, if in the slightest excess, are distinctly poisonous. Strontium is not in itself a poison, but its compounds rarely occur in nature absolutely free from barium salts.

The limit fixed in certain counties for the toleration of gypsum in wine (=2 grms. potassium sulphate per litre) seems too lax. The true standard would be the condemnation and destruction of all wines containing more sulphuric acid (free and combined) than is naturally present in grape juice. It is said that an addition to wines of calcium phosphate produces all the good results alleged to be obtained by “plastering” without its disadvantage.

Dr. Thorpe's great work carries with it its own emphatic recommendation. It must prove most valuable, not merely to chemists and chemical manufacturers, but to all merchants who have to deal with chemical products.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 16, April 17, 1893.

Detection of the Higher Alcohols and other Impurities in Vinic Alcohol.—Emile Gossart.—The method of analysis depends on the observation of the rollings of drops of known composition falling from the height of 1 m.m. with an interval of 30" on a meniscus of a plane slope.

The Hygroscopic Properties of Various Textile Substances.—Th. Schlöesing (Fils).—This paper cannot be reproduced without the accompanying diagram.

Contribution to the Study of the Leclanché Battery.—A. Ditte.—The author examines the behaviour of an element consisting of a rod of zinc attached to a plate of platinum and immersed in a 10 per cent solution of sodium chloride. The upper part of the zinc becomes covered with a layer of oxide, which descends along the rod and then spreads out horizontally, separating the liquid into two strata, the upper portion being alkaline and free from zinc, whilst the lower remains neutral and contains zinc chloride.

Attempt at a General Method of Chemical Synthesis. Formation of Nitro-Compounds.—Raoul Pidet.—It appears from the author's experiments that all the nitrifications of naphthalene, phenol, and toluol are profoundly modified by the methodical use of low temperatures along with the utilisation of electric energies introduced from without.

Stereochemistry of Malic Compounds and the Variation of the Rotatory Power of Liquids.—Albert Colson.—The author asserts that the derivatives of malic acid readily yield substances which are exceptions to the rule of the product of asymmetry. Such a substance is acetylmalic acid, $C_6O_6H_8$.

Iron Chlorobromide.—C. Lencrmand.—The compound in question, Fe_2Cl_2Br , is obtained by causing bromine to act very gradually upon anhydrous ferrous chloride. It forms dark crystals, green by reflected light, and very deliquescent.

Calcium Sucrates.—P. Petit.—A thermochemical paper not suited for useful abstraction.

New Soluble Ferment which Splits up Trehalose into Glucose.—Em. Bourquelot.—The author has found this ferment in a mould of *Aspergillus niger*, which may be preferably cultivated on Raulin's liquid. It is accompanied by another ferment which acts upon maltose, and which the author names *maltase*, the former ferment being *trehalase*.

Influence of the Pressure of Gases upon the Development of Plants.—Paul Jaccard.—As a general rule, the changes of pressure in the atmosphere surrounding a plant exert a considerable influence upon its development. The intensity and the nature of the phenomenon vary naturally more or less according to the species, but the general curve representing the variations of development with pressure has ordinarily two maximum points: the first, by far the most marked in the depressed air, and the second, in the compressed air; the normal pressure is, then, most frequently between the two maxima. Although the tension of the oxygen plays a preponderating part in the phenomenon, the action of the absolute pressure is also manifest. It may be said that the action exerted by atmospheric pressure within limits compatible with the existence of organisms is not the same in chlorophyllous plants as in animals.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. ix. and x., No. 7.

Copper Oxybromide Analogous to Atacamite.—J. Dupont and H. Jansen.—The authors obtain this compound by heating cupric oxide to 200° in a sealed tube along with cupric bromide.

Certain Points of Stereochemistry.—Albert Colson.—A continuation of the polemic against M. Friedel and Le Bel.

On Inuline: Pseudo-Inuline and Inulénine.—M. Tanret.—Pseudo-inuline after desiccation at 130° gave—

$$\begin{array}{l} C = 43.94 \\ H = 6.32 \end{array} \left. \vphantom{\begin{array}{l} C = 43.94 \\ H = 6.32 \end{array}} \right\} C_{192}H_{162}O_{162}.$$

It does not reduce Fehling's liquid. The composition of inulénine is—

$$\begin{array}{l} C = 43.47 \\ H = 6.48 \end{array} \left. \vphantom{\begin{array}{l} C = 43.47 \\ H = 6.48 \end{array}} \right\} C_{120}H_{104}O_{104}.$$

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. xxi., No. 3.

Determination of Slag in Puddled Irons.—L. L. de Koninck.—The author combats the objection raised by Barrow and Turner (*Journ. Chem. Soc.*) against the use of gaseous chlorine.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. viii., No. 87.

On the Metallic Carbonyls.—Ludwig Mond.—Translated from the *Journ. Soc. Chem. Ind.*

Zeitschrift für Analytische Chemie.

Vol. xxxi., Part 6.

(For some unexplained reason the issue of this concluding part of Vol. xxxi. has been delayed until after the appearance of Vol. xxxii. has commenced.)

Wine Statistics of Germany.—A continuation of an elaborate report on the wines produced in Germany, of little interest in other countries.

Method for the Quantitative Determination of Arsenic.—Helge Bäckström.—This paper will be inserted in full.

Apparatus for Reducing the Readings of the Barometer to 760 m.m.—A. W. J. Bockhout.

Arrangement for Closing Sulphuretted Hydrogen Apparatus.—Heinrich Trey.

Continuous Action Suction and Pressure Apparatus.—W. Reatz.—These three papers cannot be intelligibly reproduced without the eight accompanying figures.

Oxidising and Decolourising Action of Charcoal.—P. Cazeneuve.—Already inserted.

Composition of Glass Suitable for Chemical Vessels.—R. Weber (*Berg. und Hütten Zeitung*) gives the following composition:—

Silica	74.10
Alumina	1.90
Lime	9.75
Potassa	6.70
Soda	10.55
	100.00

The glass remained perfectly bright on exposure to air and in contact with hydrochloric vapours. A flask holding 100 c.c. on boiling in water for six hours lost 8 m.grms.

A Dialyser.—Gautier.—(From the *Bull. Soc. Chim. de Paris*.)

Recognition of the Temperature at which Petroleum begins to Evolve Gases and Vapours which may Explode on Admixture with Air.—A. Gawalowski (*Oel und Felt Industrie*).—On a sand-bath heated from below by a small flame is placed a capsule containing the substance in question. Over it is turned a cylinder of glass 8 to 10 c.m. in length, contracted at its upper end, and provided below with three notches. Through each of two of these notches passes a glass tube bent upwards below the cylinder, one of which is drawn out to a point and connected with the gas-pipe. In experiments a very small flame is allowed to burn at the point of the tube, whilst the other glass tube above mentioned introduces a direct supply of atmospheric air. As soon as the temperature is reached at which combustible gases are evolved there ensue small detonations. The temperature is read off on a thermometer which dips into the liquid. For determining the flashing-point the author fixes on the cylinder, which in this case is open above a small top-piece, and over it a cap of wire netting. The

tube conveying air is removed, and above the wire netting there is held a small gas flame until the gases ignite. If no gas is at hand a small wax taper may be used. In another arrangement, devised by the same author, which acts more accurately and also automatically, the oil is heated in a closed kettle, on the cover of which is fixed a Finkener burner. The petroleum vapours ascend in the mixing-tube of this burner and mix with the air admitted through a lateral opening. Near the upper aperture is a small flame which effects the ignition of the gaseous mixture as soon as a sufficiency of petroleum vapour is present. To the upper aperture of the burner-tube there is soldered a small hook, by means of which a valve is kept freely suspended by means of a cotton thread saturated with ammonium nitrate. At the moment when the mixture of gas and air is ignited the thread burns, the valve closes automatically and prevents the further escape of petroleum vapours from the small kettle.

Balances of Precision.—Two balances for rapid weighing have been proposed respectively by A. Collot, Fils (*Bull. Soc. Chim. de Paris*, iii., 61 and 98) and Victor Serrin (*Comptes Rendus*, cxii, 1299).

Photometric Apparatus, all for photographic purposes, have been devised by F. Hurter, E. G. Ballard, Driffield, and have been discussed by W. M. W. Abney. Particulars are not here given, but may be found in the *Journ. Soc. Chem. Industry*.

Laboratory Appliances used at the Connecticut Agricultural Station.—S. W. Johnson.—(From the *Journal of Applied Chemistry*).

Rapid Determination of Carbon Dioxide in Chimney Gases.—H. Sæger and Jul. Aaron (*Thon. Industrie Zeitung*).—The authors' method does not admit of explanation without the accompanying figure.

Measuring Instrument for Liquids.—Alex. F. Reid.—(From the *CHEMICAL NEWS*).

Backstroke Valve for Water Air-Pumps.—C. Haase (*Chemiker Zeitung*).—This paper requires the accompanying illustration.

Preservation of Constant Temperatures above the Boiling-Point of Water.—K. Ulsch (*Zeit. für Brauwesen*).—Already inserted.

A Desiccator.—F. Soxhlet (*Zeit. Angew. Chemie*).—Requires the four accompanying figures.

Water-Baths of Porcelain.—B. Fischer and W. Dittmar (*Chemiker Zeitung*).—Such water-baths are preferable to those of copper, both on account of their cleanliness and cheapness.

A Cooler.—E. Greiner (*Zeit. Angew. Chemie*).—An internal vessel is inclosed in a double glass jacket, traversed by a current of cold water.

Lixiviation Apparatus for the Determination of Fats.—F. Geisler (*Oel. und Felt Industrie*).—This paper requires the accompanying figure.

Purifying and Drying Coal-Gas.—A. Gawalowski.—For the description of the apparatus we must refer to the original. As a desiccating material the author uses burnt lime, slacked with a solution of ferric oxide, and then strongly dried.

A New Form of Flexible Tubes for Gas.—T. R. Almond (*Engineering and Mining Journal*).—A double system of wire spirals.

Bottles of Lead for Hydrofluoric Acid.—J. L. C. Eckelt (*Chemiker Zeitung*).—The bottles contain 100, 250, and 500 grms. of acid. They are mounted in blocks of wood, in which they may be conveyed after the wooden lid is screwed down.

Examination of Ammonia for Carbonic Acid.—J. Hertkorn (*Chemiker Zeitung*).—The author proposes the rule that a mixture of ammonia and lime-water should show only a slight turbidity on boiling.

MISCELLANEOUS.

An International Food-Law.—The *Chem. Zeitung* in a leader on the absence, in Austria, of any general legislation on the sale of food, raises the important but difficult question of an international agreement on sophisticated or substituted articles of food and consumption.

Alleged Occurrence of Helium.—Prof. Poplin, a Government Analyst in the United States, is said (in the *Chemiker Zeitung*) to have discovered a new element in a meteorite which he is examining. He observed in the spectroscopic lines corresponding to those observed by Prof. Angström, and referred by him to "helium"—a hypothetical element not detected in any terrestrial mineral. The *Pall Mall Gazette* of April 24 gives a similar account, and adds that the meteorite came from the direction of the constellation Perseus and fell in Missouri. It was found to contain 25 per cent of an unknown metal. In neither case is the original authority given.

The Thermo-Hydrometer.—In the determination of specific gravities serious errors will be introduced unless the temperature of the liquid is accurately taken simultaneously with the reading of the hydrometer. We have received from Messrs. Fletcher, Fletcher, and Stevenson, North London Chemical Works, one of their new Thermo-hydrometers, in which the bulb of the thermometer is blown in one piece with the bulb of the hydrometer and comes into direct contact with the liquid to be tested. The stem of the thermometer is inside the stem of the hydrometer, and the two scales being engraved on the same strip of ivory both can be read simultaneously. The thermometer scale is graduated from -10 to $+50^{\circ}\text{C}$., and the hydrometer from 1000 to 1050. To all who require frequent observations of specific gravity this instrument will be invaluable.

MEETINGS FOR THE WEEK.

- MONDAY, 8th.—Society of Arts, 8. "Mosaic—its History and Practice," by C. Harrison Townsend. (Cantor Lectures).
— Royal Institution, 5. (General Monthly Meeting).
TUESDAY, 9th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
— Royal Institution, 3. "Modern Society in China," by Prof. R. K. Douglas.
— Society of Arts, 8. "Primitive Art in Egypt," by Prof. W. M. Flinders Petrie.
WEDNESDAY, 10th.—Society of Arts, 8. "The Richmond Lock and Tidal Weir," by J. B. Hilditch.
— Geological, 8.
THURSDAY, 11th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, F.R.S.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
FRIDAY, 12th.—Royal Institution, 9. "Isoperimetrical Problems," by Lord Kelvin, Pres.R.S.
— Astronomical, 8.
— Physical, 5. "The Drawing of Curves from their Curvature," by O. V. Boys, F.R.S. "The Foundations of Dynamics," by Oliver Lodge, F.R.S.
SATURDAY, 13th.—Royal Institution, 3. "Johnson and Milton," by Henry Craik, LL.D.

We, the undersigned, JOSHUA BECK and WALLACE SHAWCROSS, Trustees of the Will of the late James Farmer, HEREBY GIVE NOTICE that we have sold the business of Chemical Manufacturers, carried on by us as such Trustees at Gorton Brook Chemical Works, Manchester, under the style of James Farmer, to John Gibson and Co., of Medlock Chemical Works, Manchester, who will, from and after the 17th instant, carry on such business for their own benefit under the style and title of "James Farmer." AND WE HEREBY GIVE FURTHER NOTICE that neither we nor the estate of the late James Farmer will be responsible for any debts contracted in respect of such business on or after the 17th instant.

Dated this 17th day of April, 1893.

Signed in the presence of
RICHARD HILDITCH, } JOSHUA BECK,
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1883 TO 1888.

NOTICE IS HEREBY GIVEN, that

THE CHEMISCHE FABRIK AUF ACTIEN (Vorm F. SCHERING), of 170, Müller Strasse, Berlin, Germany, has applied for leave to amend the Specification of the Letters Patent No. 15,404 of 1890, for "Improvements in the Manufacture of Spermine," granted to Wilhelm Majert.

Particulars of the proposed Amendments were set forth in the Illustrated Official Journal (Patents) issued on the 26th April, 1893.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of the opposition to the Amendment within one calendar month from the date of the said Journal.

(Signed) H. READER LACK,
Comptroller General.

PATENTS, DESIGNS, AND TRADE MARKS ACTS,
1883 TO 1888.

NOTICE IS HEREBY GIVEN, that

THE CHEMISCHE FABRIK AUF ACTIEN (Vorm F. SCHERING), of 170, Müller Strasse, Berlin, Germany, has applied for leave to amend the Specification of the Letters Patents No. 11,957 of 1891, for "Improvements in the Manufacture of Piperazine or Spermine," granted to Wilhelm Majert.

Particulars of the proposed Amendments were set forth in the Illustrated Official Journal (Patents) issued on the 26th April, 1893.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of the opposition to the Amendment within one calendar month from the date of the said Journal.

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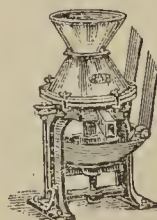
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THE CHEMICAL NEWS.

VOL. LXVII., No. 1746.

ON THE ABSORPTION-SPECTRA OF SOME COMPOUNDS OF CHROMIUM.*

By W. LAPRAIK, Ph.D., F.I.C.

(Continued from p. 209).

Croft's Red Potassium Chrom-Oxalate (5),
 $K_2Cr_24C_2O_4 + 8H_2O$ or I_2H_2O .

I NOW made some of this salt according to Croft's directions. By the action of fifty-five parts by weight of crystallised oxalic acid on a solution containing nineteen parts of potassium dichromate, then evaporated to small bulk and put aside to crystallise, after the lapse of several weeks the salt was obtained. The crystals were dissolved in water, and gave the following absorption-spectrum (5).

Continuous absorption ending about 800, then a faint shadowy band at 710; then two thin dark bands having their centres at 704 and 695 respectively; then two faint incidental bands at 681 and 663 respectively. The broad absorption from 633–502, and continuous absorption from about 467.

It would thus appear that this spectrum with the dark double lines at 704 and 695 is typical of the salts of the formula $M_2'Cr_24C_2O_4$. Now, it has been shown that this is the absorption-spectrum given by the first action of oxalic acid on a solution of chromium oxalate, and which for the reasons mentioned previously is undoubtedly the absorption-spectrum of the hydrogen compound of the series $M_2'Cr_24C_2O_4$.

Further, it has been shown that with more oxalic acid and when the solution is heated the band 695 disappears, while the remaining incidental bands together with the dark band at 704 become darker, and we have an absorption-spectrum identical with that given by the salts of the general formula $M_6'Cr_26C_2O_4$. Now since in neither case is there present any metal corresponding to M' , but hydrogen only, it follows that the absorption-spectrum given must be due to the hydrogen compound of this series.

The constitution of these two series of salts— $M_6'Cr_26C_2O_4$ and $M_2'Cr_24C_2O_4$ —is not that of double salt, as in that case their absorption-spectra would not differ from that of chromium oxalate, but is rather that of salts of two acids— $H_6Cr_26C_2O_4$ and $H_2Cr_24C_2O_4$ respectively. It is for this reason that these compounds have been designated chrom-oxalates throughout this paper.

Other Analogous Oxalates.

It is well known that the double oxalates of the alkalis with iron, manganese, and cobalt possess exceptional colours; thus the ferric salts are usually yellow, while potassium ferric oxalate has a fine green colour resembling the ferrous salts. Again, the cobalt salts are either blue when anhydrous or red when hydrated, while potassium cobaltic oxalate has a beautiful green colour not unlike the colour of nickel salts.

With the above facts in view, and also what has been already stated relative to the constitution of the chrom-oxalates, it was thought desirable to study the spectroscopic relations of these compounds.

The double ammonium and potassium salts of ferric, manganic, cobaltic, and cupric oxalates were prepared and spectroscopically examined.

Ammonium Ferric Oxalate, $(NH_4)_6Fe_26C_2O_4 + 6H_2O$
(No. 6).

This salt was dissolved in water, and a layer of the solution having a thickness of 6.4 c.m. was examined.

This gave continuous absorption to 698, shading off to 623, and then continuous absorption from 489 to the end of the spectrum (6).

It is known that this salt, together with others, is decomposed by light, and some experiments were made to determine the limits of the more active rays effecting this decomposition. Glass tubes containing the salt in solution were put into clear colourless glass bottles, the latter containing respectively concentrated solutions of the following bodies:—Ammonium copper sulphate, potassium dichromate, ammonium ferric oxalate (which was frequently changed as it became decomposed), and copper chloride. The bottles and tubes were then securely covered with opaque paper which reached just below the surface of the liquid in the outer vessel, so that the only light which penetrated to the tube containing the solution under experiment passed through a protecting layer of the above solutions, having a thickness of 2 c.m. The absorption-spectrum given by a layer of this thickness of protecting liquid was then determined, with the following result:—

	Continuous absorption.	Continuous absorption.
1. Ammonium copper sulphate ..	500	418
2. Potassium dichromate	717	543
3. Cupric chloride	608	480
4. Ammonium ferric oxalate ..	698	465

The ammonium ferric oxalate solution under experiment was completely decomposed after standing in (1), ammonium copper sulphate after two days exposure to sunlight.

In (2) potassium dichromate solution no decomposition occurred even after standing five days.

In (3) cupric chloride very slight decomposition resulted after standing five days.

In (4) ammonium ferric oxalate there was a greater amount of decomposition than in the case of (3) after standing the same time, viz., five days.

From these experiments the more active rays are those lying between 480 and 418.

It is worthy of note that these rays, which were transmitted by the above thickness of ammonium ferric oxalate, were still able to produce a certain amount of decomposition in that salt, although the protecting layer of ammonium ferric oxalate was frequently changed as it was decomposed. These experiments were made in the summer months.

Potassium Ferric Oxalate, $K_6Fe_26C_2O_4 + 6H_2O$.

This salt gave in solution a similar absorption-spectrum, continuous absorption to 698, then a slight shadow to 627, and continuous absorption again from 489.

The crystals of this salt were also examined, but no definite bands could be observed.

In order to see if ferric oxalate behaved differently when dissolved in oxalic acid, the experiment was made, and it was found that there was much less absorption in this case in the less refrangible part of the spectrum, the continuous absorption reaching only to 790, as compared with 698 in the double salt.

Potassium Manganic Oxalate, $K_6Mn_26C_2O_4 + 6H_2O$ (7).

This was the next salt examined. It is easily made by the action of manganese dioxide on a solution of acid potassium oxalate. It is very unstable, and requires to be examined immediately. The solution was of a fine dark red colour, but no absorption bands were observed, only continuous absorption from 704 and 601 respectively.

The corresponding ammonium salt gave the same absorption-spectrum.

Potassium Cobaltic Oxalate, $K_6Co_26C_2O_4 + 6H_2O$ (8).

This salt has been fully described by Kehrman and Pickersgill (*Ber.*, xxiv., 2324, 1891) as crystallising in nearly black prisms, which are dichroic—blue and green.

* *Journ. für Prakt. Chemie*, xlvii., 305 (1893).

It yields a fine dark green solution, which gives a broad absorption band in the green part of the spectrum. My measurements are as follows:—Continuous absorption to 770, with a shadow to 710; then a broad absorption band from 657 to 543, and continuous absorption from 469.

Potassium Cupric Oxalate, $K_2Cu_2C_2O_4 + 2H_2O$ (9).

This salt was next examined; it yields a blue solution like the other cupric salts; a thickness of 9.2 c.m. of solution was used in examining its absorption-spectrum. In this case also no absorption bands were visible, only continuous absorption to 639 and from 411. The crystals of this salt were also examined, but with a similar result as the above. The same remark applies to the ammonium salt, which was also examined.

As the foregoing oxalates have now been shown not to give characteristic absorption-spectra, it is therefore impossible to determine their constitution by the same spectroscopic methods which have been used for the corresponding chrom-oxalates, but I thought that the results obtained were worth recording.

Analogous Compounds with Malonic Acid.

Having shown how the various chrom-oxalates are related spectroscopically to each other, to chromium oxalate, and also to the analogous oxalates of other metals, it was thought desirable to search for similar compounds in the case of various organic acids. The first which naturally suggests itself is the homologue of oxalic acid, viz., malonic acid.*

In the following experiments the acid was allowed in some cases to act in the cold on an excess of chromium hydroxide. In other cases the acid was in large excess, and heat was applied, when that was possible without decomposition.

Various specimens of chromium hydroxide were prepared, and precautions were taken to have it free from fixed alkali. Thus pure chromium trioxide dissolved in water was reduced by alcohol and precipitated by ammonia solution in excess. The resulting precipitate of chromium hydroxide was well washed by decantation, and thrown on a filter, and again well washed. This was re-dissolved in hydrochloric acid and re-precipitated, as before, by ammonia solution, and washed till the washings gave no precipitate with a solution of silver nitrate acidified with nitric acid. Duplicate experiments were made; in all cases using a different specimen of chromium hydroxide. In some other cases, another specimen of the acid was procured from an entirely different source, but with a like result in all cases.

Malonic Acid, $CH_2(CO_2H)_2$ (11).—A strong aqueous solution of this acid easily dissolves freshly precipitated chromium hydroxide. The solution has a fine bluish purple colour, and gave the following absorption-spectrum:—

Continuous absorption to 714, then a band from 695—689, then a shadow from 655 joining the broad absorption from 623—503, and continuous absorption from 464.

On comparing this spectrum with that given by chromium oxalate, it is similar in character, but does not appear to be identical with it; for, as the result of repeated observation, the centre of the band in the red part of the spectrum is moved slightly nearer the more refrangible end. It is also somewhat darker, while the broad absorption appears about the same in both.

An excess of malonic acid added to this solution does not appear to influence the absorption-spectrum. In this respect also it differs from oxalic acid in its action on chromium oxalate.

A little ammonium malonate was now added to the solution of chromium hydroxide in malonic acid, and the solution warmed. The resulting solution gave an absorption spectrum differing from the above, but similar

in character to that given by the chrom-oxalates of the general formula $M'_6Cr_26C_2O_4$, and from this it was believed that a similarly constituted compound was produced. The ammonium malonate was, in another experiment, replaced by potassium malonate, with a like result spectroscopically. It was found that the ammonium salt did not crystallise so well as the potassium salt, therefore some quantity of the latter was prepared, by the action of an excess of freshly precipitated chromium hydroxide on a solution of acid potassium malonate. The action takes place easily if the chromium hydroxide is freshly precipitated. This solution gives an extremely dark band, its centre being 701.

If an excess of the acid has been used, or what is the same thing, if the chromium hydroxide is not in sufficient quantity, or if it has been insufficiently digested, two dark bands in the red part of the spectrum appear, as is the case with the oxalate under similar conditions. Two hours digestion was usually found sufficient. It was then filtered, evaporated to small bulk, and it was then placed over sulphuric acid, when the salt crystallised out. As it is extremely soluble in water, it is somewhat difficult to crystallise. In some cases, when the crystallisation was imperfect, the crystals were washed with alcohol.

The salt was analysed and the following numbers obtained:—

Grm.	At 120° C.	Grm.	P.c.	P.c.
0.7865	lost	0.0812	= 10.32 H_2O	
0.7865	gave	0.1200 Cr_2O_3	= 15.24 Cr_2O_3	= 10.45 Cr
1.2532	gave	0.1839 Cr_2O_3	= 14.66 Cr_2O_3	= 10.06 Cr
1.7030	gave	0.2540 Cr_2O_3	= 14.97 Cr_2O_3	= 10.30 Cr
0.6810	gave	0.2787 KCl	= 40.93 KCl	= 21.47 K

$K_2Cr_26(C_3H_3O_4)_6 + 6H_2O$			Found.		
Calculated.					
K..	..	22.15	—	—	21.47
Cr	..	9.82	10.06	10.30	10.45
H_2O	..	10.19	—	—	10.32

There can be little doubt that this is a salt of malonic acid analogous in composition to the corresponding oxalic acid compound. Like that body it is a dichroic—green and blue. Seen under the microscope, the crystals of the salt appear of a very fine green colour, or of a deep indigo blue colour, according to the axes along which the light is transmitted. The salt is green by daylight, but reddish blue by lamplight. The crystals are intensely coloured, so much so that only the thinnest crystals allow light to be transmitted, which by lamplight is of a reddish blue colour. The salt is very soluble in water, but insoluble in alcohol. When silver nitrate is added to a solution, a gelatinous precipitate of a reddish blue colour is obtained which is the corresponding silver salt. This body is but slightly soluble in cold, but more soluble in hot water. The absorption-spectrum of the silver compound is the same as that of the potassium salt. Calcium chloride gives no precipitate when added to a solution of potassium chrom-malonate.

The crystals obtained by slow evaporation were larger, and were examined for their absorption-spectrum. It was found more convenient to mount them between glass, using Canadian balsam as a cement. The absorption-spectrum thus given was similar to that produced by crystals of the corresponding potassium chrom-oxalate.

The principal absorption-band in the red part of the spectrum is, however, noticeably darker and sharper. It is further remarkable as being distinctly nearer the blue end of the spectrum; and further, what frequently appeared as a shadow in former absorption-spectra, now appears in the case of this salt as a distinct band at 655. The absorption spectrum (10) of the crystals of this salt is as follows:—

A faint thin band at 714; a very dark and sharp band at 701. Then two faint bands at 681, and 660 respectively; further, another faint band at 655, which joins the broad

* This and the other organic acids used were obtained from Kahlbaum, Berlin.

absorption ending at 507; and, lastly, continuous absorption from 465.

A solution of the salt in water is of a reddish blue colour and gives an absorption-spectrum exactly the same as that given by the crystal. The only difference is that the bands 681, 660, and 655 are less distant and less sharp.

When an excess of malonic acid is added to a solution of potassium chrom-malonate, two dark sharp bands are seen in the red part of the absorption-spectrum instead of one. These bands are slightly nearer the blue end of the spectrum as compared with those given by a solution of the salt $K_2Cr_24C_2O_4$, but in other respects the absorption-spectra are similar.

It would thus seem not unlikely that there is thus formed a compound of malonic acid analogous to the salt $K_2Cr_24C_2O_4$, but I have not succeeded in separating it.

Having now shown that there exists a double compound of potassium and chromium with malonic acid, analogous in composition, properties, and absorption-spectrum with the corresponding salt of oxalic acid, I naturally tried the next acid of the same series—succinic acid—by exactly the same method that enabled me to obtain the potassium chrom-malonate. I digested a portion of the specimen of chromium hydroxide which was used for making the malonic acid compound, and which was freshly precipitated with a solution of acid potassium succinate; the chromium hydroxide did not dissolve, nor was the solution in any way coloured. I then attempted to dissolve the chromium hydroxide in a concentrated aqueous solution of succinic acid. After prolonged heating a small quantity dissolved.* The solution had a green colour by daylight and a reddish colour by lamp-light. It therefore differed in colour from the double salts which I had previously examined, and, as was to be expected, its absorption-spectrum was also different (12). It is characterised by having two dark bands 727—715 and 679—670 respectively. These absorption-bands are not so dark nor so sharp as the principal band in the red part of the spectrum given by the previously mentioned compounds of oxalic and malonic acids. Between these bands are two others, somewhat fainter but fairly sharp at 707 and 693 respectively. There is also another band at 655 which is rather difficult to see, as it is joined to the broad absorption which extends from 644 to 537, and, lastly, continuous absorption from 498.

The whole character of this absorption-spectrum is quite different from those previously described. It is more nearly related (as will be subsequently shown) to that given by the fatty acids when they are treated in the same way. I endeavoured to obtain a double salt in this case also, but my efforts were not successful, one reason being that the amount of chromium compound in solution was small.

(To be continued).

INSTRUCTIONS FOR THE EXAMINATION AND JUDICIAL DECISION ON PORTIONS OF ANIMAL ORGANISMS INTENDED FOR HUMAN FOODS.†

By WILHELM EBER.

WITH death decompositions set in in parts of the animal body, when portions of freshly-slaughtered animals are poorer in colouring-matter than they are subsequently. The muscles on access of air take a fuller yellowish-red colour; the liver and kidneys become a darker brown under the same circumstances. All other parts take a more or

less decided admixture with yellow, which is particularly intense in the case of cattle which have been pasturing. The reaction of animal matter shortly after slaughtering is alkaline, and in the muscles, on the occurrence of coagulation, it becomes amphoteric, or slightly acid; this is *simple acidification*. Portions of the animal body may then by the development and action of ferments and septic organism pass into *acid fermentation* or into putridity, or into mixed processes of these two typical kinds of decomposition. The acid fermentation in substances which are rich in carbohydrates (liver and muscles) connects itself with simple acidification if sufficient moisture is present.

In large pieces of meat, suitably kept, it attains a high degree, and in its later stages it is characterised by the diminished power of the pigments of the muscles to assume a bright scarlet colour in contact with air. In the liver the dark brown pigment is changed by the acid fermentation to a light brown. The *rigor mortis* decreases under the influence of the acid fermentation, the meat becomes more tender and takes a pleasant acidulous odour. This process is called in lay circles "ripening," and the meat is said to have been "thoroughly killed."

In the subsequent stages of acid fermentation (fourteen days to three weeks) the muscular flesh, along with traces of hydrogen sulphide, contains a peculiar aromatic flavouring matter (*haut goût*). *Haut goût* is not a product of putrefaction.

Under especial conditions acid fermentation is accompanied by intensely stinking products. It is then called offensively *acid fermentation*. It occurs, e.g., in the muscular tissues of game, which is dispatched in large quantities before it has lost its vital heat. The putrid products generally contain very much hydrogen sulphide. The pigment of the muscles assumes on the surface of fresh sections a colour from greyish green to leaf-green. Bubbles of gas may occur in the tissues.

Simple acidulation, acid and offensively acid fermentation, may be overpowered by true putrefaction. *Putrefaction is ammoniacal fermentation*. Free ammonia is always formed from albuminous and gelatigenous substances along with poisonous bases, fixed or volatile. The starting-point of putrefaction is the inter-muscular connective tissue. The true muscular fibre may, therefore, under some circumstances retain its acid reaction notwithstanding energetic putrefaction. Striking changes of colour appear only on those parts of hæmoglobiniferous objects which are exposed to the air and are by no means characteristic of putrefaction. Substances of putrid odour may be formed in putrescent substances, but are very often wanting (e.g., in decomposing sausages). We must therefore discriminate between stinking and non-stinking putrefaction. For recognising putrefaction the author uses the alkaline reaction and tests for ammonia (see below).

The examination of meat is conducted as follows:—

1. The article is weighed, and if it has been refrigerated it is brought to the temperature of the room. We determine its form, the presence or absence of *rigor mortis*, and its state of nutrition.

2. Appearance of the free surfaces.

(a) The colour is observed in ordinary diffused light, in reflected light (lustre, phenomena of interference), and in the dark (phosphorescence). The transparency of the tissues is tested.

(b) Proportion of moisture, and if necessary coatings (mould adhesive paste). The colour of any coating upon a coloured ground can be determined only after a portion has been spread upon white paper.

(c) Odour: the decision should, if possible, be made by several persons. For demonstrating hydrogen sulphide a specimen of the object in question is put in a wine glass, the mouth of which is covered with a piece of white paper, on the under surface of which is placed a drop of solution of lead acetate. This drop is examined every five minutes (without raising the paper), and the obser-

* The chromium hydroxide must be freshly precipitated, as on standing it quickly becomes insoluble in succinic and other weak acids.

† From the *Zeit. Anal. Chemie*.

vation is completed in fifteen minutes. The drop is coloured pale brown or black according to the quantity of hydrogen sulphide.

(d) The ammonia test, with at least five portions of the free surfaces. For this test the author uses two test glasses of equal width (having feet). One glass can be closed with a solid caoutchouc stopper, and the other with a perforated stopper of the same material. The perforation admits a glass rod, which projects into it beyond the middle of the test glass.

Each of these glasses is charged to the depth of 1 c.m. with the following reagent:—Pure hydrochloric acid one part, three parts alcohol at 96 per cent, one part ether. Pure hydrochloric acid forms a grey mist even with watery vapour, and is therefore not suitable for the detection of minute quantities of ammonia in moist bodies. The glasses are then closed with their stoppers, and the glass with the solid stopper is moved as if we wished to heat its contents over a flame. But the liquid must not be made to move more than 1 c.m. above its original level. The glass is thus filled with the colourless vapours of the mixture of HCl, alcohol, and ether. Small quantities of the substance under examination are then peeled or scraped off and fixed on the glass rod of the perforated stopper. The solid stopper is then cautiously twisted out of the test-glass, and the charged glass rod is immersed in the test-glass so as not to soil the sides of the latter, and the portion of meat remains at the distance of from 1 to 2 c.m. from the surface of the liquid.

If no clouds appear—which is best observed if the glass is viewed against a dark background with the light from above—there is no ammonia present, and consequently no putrefaction. In presence of ammonia in all cases grey, smoke-blue, or white mists descend from the object to the surface of the liquid after having at first enshrouded the specimen. After the observation has been completed, the stopper with the rod is removed and the solid rod is re-inserted.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

FIRST PAPER: THE ANALYSIS OF BARIC BROMIDE.

By THEODORE WILLIAM RICHARDS.

Introduction.

IN the course of a recent determination of the atomic weight of copper (*Proc. A. A. A. S.*, xxvi., 258), there was an attempt made to determine the ratio of cupric to baric sulphate; but in the discussion of the result it became evident that the ordinary method of precipitation was far too crude for the desired purpose. Moreover, even had there not been possible errors of a serious nature in the method, the atomic weight of barium was evidently too uncertain to form the basis of any accurate comparison. Hence this attempt was at the time given up, and the plausibility of the single result obtained was ascribed to a chance elimination of opposite errors.

During the early part of this century, a number of chemists have investigated the atomic weight of barium with very widely varying results. The first experiments worthy of mention were made by Berzelius and Klaproth (see Wollaston, *Phil. Trans.*, 1814, p. 20), but these are now of historical interest only. In 1818 the problem was again undertaken by Berzelius (*Pogg. Ann.*, viii., 189), who found that from 100.00 parts of anhydrous baric chloride he could obtain 138.07 parts of argentic chloride, whence the atomic weight is readily computed to be

136.8. At the same time he found that the same amount of baric chloride yielded 112.175 parts of baric sulphate, which gives $Ba = 135.6$.

In 1829 Edward Turner (*Phil. Trans.*, 1829, p. 296), published a re-determination of the latter ratio, finding the equivalents to be as 100.00 : 112.19. He, too, weighed the argentic chloride obtainable from a given amount of baric chloride, and arrived at the conclusion that the atomic weight of barium could not be far from 137.45. Two years later T. Thomson (*"System of Chemistry,"* 7th Edition, 1831, I., 426) described several attempts to weigh barium as the sulphate, which need not be further discussed. In 1833 Turner (*Phil. Trans.*, 1833, p. 538) found as a mean of three experiments that 112.03 parts of baric nitrate were required to form 100.00 parts of baric sulphate,—a result indicating 137.0 as the atomic weight of barium. Ten years later Salvétat (*Comptes Rendus*, xvii., 318) published a very incomplete account of the quantitative study of the conversion of baric carbonate into sulphate, giving a final result of 136.

Soon after this both Pelouze (*Ibid.*, xx., 1047) and Marignac (*Liebig's Annalen*, 1848, lxxviii., 215) determined the ratio of baric chloride to metallic silver, the first finding the atomic weight of barium to be 137.3, and the second 137.1. In 1850 Levol (*Ann. Chim. Phys.*, [3], xxx., 359) reduced auric chloride with sulphurous anhydride, and determined the sulphuric acid which resulted with baric chloride. Re-calculated with the recently determined atomic weight of gold, 197.3 (Krüss, 1887; Thorpe and Laurie, 1887; and Mallet, 1889), these results give 138.3 as the atomic weight of barium. In the next year H. Struve (*Liebig's Annalen*, 1851, lxxx., 204) found that 100 parts of baric chloride produced 112.094 parts of baric sulphate,—a value which leads to an atomic weight of barium equal to 137.0. T. Andrews (British Association Report, 1852, Part II., p. 33) obtained in 1852 the value 137.6, but he gives none of his details. Six years afterwards Marignac (*Liebig's Annalen*, cvi., 165) re-determined the ratio of baric chloride to the sulphate, with a result very different from those of his predecessors. In his hands 100 parts of the former salt yielded only 112.011 parts of the latter, instead of 112.09 or more. In the same investigation he determined the amount of water of crystallisation in baric chloride, with results so unsatisfactory that the values calculated from the various ratios varied from 128.5 to over 138 (see Meyer and Seubert's "Atomgewichte," p. 176), as well as the ratio of baric chloride to metallic silver. This last determination led to a value for barium only four $\frac{1}{100}$ ths of a unit higher than his previous work ten years before. He admits that the substances used in the analysis were not perfectly pure, but assumes that the impurities were not great enough seriously to influence the result. At about the same time Dumas (*Liebig's Annalen*, cxiii., 22) was also determining the ratio of baric chloride to silver. He fused the salt in a stream of hydrochloric acid gas, but gives no proof that a slight excess of the gas was not absorbed. If this had been the case, of course the observed atomic weight of barium would have been too low. As a matter of fact, he obtained 137.0 for the value of this "apparently variable constant." Below is tabulated a list of the various determinations, grouped according to the processes employed.

The Atomic Weight of Barium.*

O = 16.000.

Analysis of baric carbonate:—

Berzelius, 1811	Ba = 134 to 143
Wollaston and Klaproth, 1814	139.2
Salvétat, 1843	136

* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

* The writer is much indebted to the works of Becker, Clarke, Meyer and Seubert, and Ostwald for valuable assistance in preparing this list.

Conversion of baric chloride to sulphate:

Berzelius, 1818.. .. .	Ba=135.6
Turner, 1829	Ba=135.4
Thomson, 1831.. .. .	Ba=136 $\frac{1}{2}$
Struve, 1851	Ba=137.0
Marignac, 1858.. .. .	Ba=138.5

Conversion of nitrate into sulphate:

Turner, 1833	Ba=137.0
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Comparison of baric sulphate with gold:

Levol, 1850	138.3
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Ratio of baric chloride to argentic chloride:

Thomson	Ba=136 $\frac{1}{2}$
Berzelius, 1818.. .. .	Ba=136.8
Turner, 1829	Ba=137.4
Marignac, 1858.. .. .	Ba=137.1

Ratio of baric chloride to silver:

Pelouze, 1845	137.28
Marignac, 1848.. .. .	137.11
„ 1858.. .. .	137.15
Dumas, 1859	137.00

Ratios including water of crystallisation:

Marignac, 1858 (averages) ..	130.7 to 138.5
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Unknown ratio:

Andrews, 1852	137.6
Clarke, 1883, selects*	Ba=137.0
L. Meyer and Seubert, 1883, select ..	Ba=137.2
Ostwald, 1885, selects	Ba=137.04
Van der Plaats, 1886, selects.. .. .	Ba=137.1

A cursory glance at the list will show a lamentable lack of consistency in the results of even a single method in different hands. The only ratio which seemed capable of yielding approximate results was the ratio of baric chloride to metallic silver, and here the variations in the atomic weight of barium amounted to nearly three-tenths of a unit. The question whether the errors were due to mechanical defects of analysis, or to admixture of foreign substances, became an important subject for consideration; but it is evidently of little use to re-calculate such heterogeneous results. The necessity for a careful experimental revision is very apparent. Such a revision would be especially interesting in view of the fact that barium is a member of one of the best marked series of elements known,—a series which might yield important information regarding a possible mathematical relation of the atomic weights. Moreover, the atomic weights of no less than eighteen other elements† have been determined, at one time or another, by reference to baric sulphate. Most of these determinations have been made without the least precaution with regard to the baric chloride occluded in the precipitated sulphate, or on account of the solubility of the sulphate itself; but even if the method had been satisfactory, the determinations could not be considered as anything more than crude approximations, because of our uncertainty regarding the molecular weight of baric sulphate.

These were some of the considerations which prompted the present undertaking. It is not unnatural that the revision should have been begun with the more or less strong belief that the atomic weight of barium could not be far from 137.1; but the progress of the work has completely overthrown this belief, and has indicated a much higher value.

(To be continued).

Mica.—Messrs. Wiggins and Sons have again obtained the Admiralty contract for the supply of Mica.

* In Clarke's original treatise 137.007 is apparently misprinted for 137.07 (Smithsonian Misc. Coll., vol. xxvii., p. 63).

† Li, Be, F, Mg, Si, V, Cr, Ni, Cu, Se, Y, In, (Ba), La, Ce, Di, Au, Ti, Th.—Compare L. Meyer and Seubert's "Atomgewichte," p. 105.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 20th, 1893.

Dr. ARMSTRONG, President, in the Chair.

MR. WM. E. WHEELER was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Henry Bailey, 18, Lavender Sweep, London; Douglas S. P. Berringer, B.A., Malvern College, Malvern; John Henry Coste, 69, Goswell Road, E.C.; Arthur Henry Green, 176, Lloyd Street, Greenheys, Manchester; Charles Mills, Hazeldean, Fulham Park Gardens, S.W.; Alexander Orr, 109, Pitt Street, Sydney, Australia; Charles Herbert Pring, The Ferns, Longfield Road, Bristol; George Ritchie, 8, Buchanan Gardens, Mount Vernon, N.B.; Henry Thomas Sorrell, Holly Lodge, Hill, Southampton West; Sydney Whalley, 38, Havelock Street, Canterbury; Thomas Whittaker, 76, Arden Terrace, Accrington.

Of the following papers those marked * were read:—

*1. "A Contribution to the Chemistry and Physiology of Foliage Leaves." By HORACE T. BROWN, F.R.S., and G. HARRIS MORRIS, Ph.D.

The investigation relates to the occurrence, relations, and physiological significance of the starch, diastase, and sugars contained in foliage leaves.

The authors divide the subject into two parts; the first, dealing with the starch and diastase of leaves, is subdivided into the following sections:—(1) Introduction; (2) Historical; (3) The Starch of the Leaf, its Determination, and the Proportion it bears to the Total Products of Assimilation; (4) The Occurrence of Diastase in the Leaf; (5) The Nature of the Products of Transformation of Starch by Leaf-Diastase; (6) The Determination of the Diastatic Activity of Leaves; (7) The Periodic Variation of the Diastase of Leaves; (8) Can Leaf-Diastase Act on Solid Starch? (9) How Far is the Disappearance of Leaf Starch due to Living Protoplasm? The second part treats of the sugars of the leaf, and consists of an historical section, and one dealing with the sugars of *Tropaeolum majus*. The bibliography of the subject is summarised in an appendix.

The work originated in an attempt to discover the explanation of the conditioning effect of "dry-hopping," i.e., the addition to finished beer of a small amount of dry hops. This was ultimately traced to the presence in the hop-strobiles of a small, but appreciable, amount of diastase, sufficient to slowly hydrolyse the non-crystallisable products of starch transformation left in the beer, and to reduce them to a condition in which they can be fermented by the yeast. In endeavouring to ascertain if this occurrence of diastase in the hop-strobile was an isolated case, or a special example of a widely distributed property of vegetable tissue, the authors were led to enquire into the first formation of starch in the chloroplasts of the foliage leaf, the mode of its dissolution and translocation in the plant, and the nature of the metabolised products.

The results obtained are regarded as entirely antagonistic to the assumption made by Sachs, that all the products of assimilation at some time take the form of starch.

Using the half-leaf gravimetric method devised by Sachs, the authors confirm his results as to the rate of assimilation, but they show that only a small portion of this assimilated material exists at any one time in the form of starch.

The starch in leaves was estimated by hydrolysing it, with suitable precautions, with the aid of diastase, and then determining the products of its hydrolysis in the

usual way by means of the polarimeter and Fehling's solution. The fluctuations in the amount of starch in leaves under various conditions, and also in leaves plucked at different times in the day, have been determined by this method.

It is shown that Wortman's recent denial that diastase plays any part in the dissolution and translocation of starch in leaves is incorrect. The authors prove that, instead of leaves containing little or no diastase, every leaf examined by them contained sufficient diastase to transform far more starch than the leaf can have contained at any one time; in many cases sufficient diastase was present to hydrolyse an amount of starch many times the total dry weight of the leaf. The difference between the authors' and Wortmann's results is chiefly due to the fact that whereas Wortmann examined the clear filtrate obtained by macerating the crushed leaves in water during a few hours, they have digested the air-dried and powdered leaf itself with soluble starch solution.

It is further shown that the products of the hydrolysis of starch by leaf diastase are identical with those formed by malt diastase, maltose having been directly separated from the leaves, and its optical and reducing properties determined. Leaf diastase is not able to convert maltose into dextrose, but the leaf contains an enzyme capable of inverting cane-sugar.

In the course of a large number of comparative determinations of the diastatic activity of various leaves, it was found that the amount of diastase varied greatly in different plants, and within narrower limits even in the same plant at different times. It is very high in the case of the Leguminosæ, the diastatic activity of *Pisum sativum* being between one-half and one-third of that of an average pale barley malt.

An attempt to ascertain if the fluctuations in diastase were in any way periodic, or were governed, as are the fluctuations of starch in the leaf, by any external conditions, showed that any conditions which favour a decrease in the leaf starch result in an increase of the leaf diastase; for instance, leaves kept in darkness, either on or apart from the plant, show a marked increase in diastatic activity. In view of the results obtained in their former paper on the "Germination of the Gramineæ" (*Trans.*, 1890, 458), the authors explain this by the assumption that as long as the conditions favour assimilation, the leaf cells are necessarily supplied with an abundance of newly assimilated materials in the form of sugars, more, in fact, than can be easily made use of or translocated, the excess of nutritive material being in part deposited as starch. At this period there is little or no elaboration of diastase by the cell protoplasm, probably none at all in those cells in which starch deposition is actually going on. When the light fails and assimilation consequently falls off, the living cells speedily use up or translocate the excess of assimilated products, such as cane-sugar, and begin to draw their supplies from the more permanent starch. To enable the cells to do this effectually, the somewhat starved protoplasm now commences to elaborate the needed diastase more rapidly, and the secretion of the enzyme becomes accelerated as the starvation point of the cell is reached, the secretion of diastase by the leaf cell being, in fact, like that of the embryo of the grasses, to some extent a *phenomenon of starvation*. Experiments confirmed this view.

Contrary to Wortmann's statement, it was found that under certain conditions leaf diastase can attack the solid starch granule; but attempts to obtain any evidence of the disappearance under the influence of the contained diastase of starch in killed leaves gave negative results, and the authors are led to the conclusion that the *first stage* of dissolution of the starch granule in the leaf is in some way or other bound up with the *life* of the cell. When, however, all the facts are considered and due weight given to (1) the constant and abundant occurrence of diastase in leaves, (2) to the apparent correlation of this diastase with the occurrence of starch, (3) to the

remarkable periodicity of the rise and fall of diastase, and (4) to the correlation of this periodicity with the appearance and disappearance of starch, it is impossible to accept Wortmann's view that the dissolution of starch in the leaf is in no way conditioned by a starch-dissolving enzyme. On the contrary, the authors believe that their experiments establish beyond all doubt the physiological importance of diastase as an active agent in the dissolution and translocation of starch, not only in leaves, but also in the growing parts of all plants. As further evidence of this, the authors adduce the fact that *maltose* was found amongst the sugars of the leaf when the starch was disappearing.

Selecting the leaves of *Tropæolum*, experiments were carried out to ascertain the nature of the leaf sugars and the variations in amount and relative proportions at different times, and also for the purpose of throwing some light on the relation which each sugar bears to the primary assimilation products on the one hand, and to the leaf starch on the other, *i.e.*, to ascertain which are the true "up grade" sugars from which starch is formed, and which are the "down grade" sugars resulting from the hydrolysis of starch.

The only sugars found were *cane-sugar*, *dextrose*, *levulose*, and *maltose*. The total amount of the sugars is subject to great variations, and the relative proportion which they bear to each other is also very varied. The results obtained lead to the following conclusions:—Cane-sugar is the first sugar to be synthesised by the assimilatory processes. This sugar accumulates in the cell sap of the leaf parenchyma when assimilation is proceeding vigorously, and when the concentration exceeds a certain point starch commences to be elaborated by the chloroplasts at the expense of the cane sugar. This starch forms a more stable reserve material than the cane-sugar, and is only drawn on when the latter more readily metabolised substance has been partially used up. Cane-sugar is translocated as dextrose and levulose, and the starch as maltose. From the invert sugar derived from the cane sugar, the dextrose is more readily used up for the respiratory processes, and possibly also for the new tissue building, than is the levulose; hence in a given time more levulose than dextrose must pass out of the leaf into the stem.

DISCUSSION.

The PRESIDENT, after remarking that a more suggestive paper had never been brought under the notice of the Society, referred to the statement made by the authors regarding the origin of the research as a striking illustration of the advantage to be derived from the association with our manufacturing industries of thoroughly qualified scientific men. A research originally commenced with the object of explaining a common brewery practice had not only afforded the required information, but in addition improved methods of analysis had been devised in the course of the work; and facts had been discovered which ultimately might serve as the basis for the interpretation of the manifold changes involved in the formation and degradation of carbohydrates in plants, and which also might largely contribute to the solution of purely theoretical problems concerning the nature of the carbohydrates. He was not prepared to allow the interpretation of the manner in which cane-sugar was formed that had been put forward by Messrs. Brown and Morris to pass unchallenged. On a previous occasion, when discussing their paper on the "Germination of the Gramineæ," he had suggested that perhaps cane-sugar was formed from maltose, and not from dextrose and levulose, to unite which all attempts hitherto made had failed; that, in fact, one of the dextrose residues of maltose was converted into levulose, and that the compound thus formed underwent a change—an internal condensation—resulting in the production of cane-sugar, the nature of which even yet is not understood, but which, apparently, does not contain aldehydic groups. The evidence now brought forward was, he thought, compatible with this view.

Such a passage from maltose to cane-sugar would be of advantage to the plant, as it would then have at disposal a material that was hydrolysed more easily than maltose; the superior nutritive value of cane-sugar might be due at least partly to this fact. Levulose perhaps played a special part in certain metabolic processes; it was well known to be much more sensitive than dextrose towards hydrolytic agents, the formation of levulinic acid being an instance of this, and it was not improbable that it was therefore of superior value in comparison with dextrose and other carbohydrates, because able to take part in some of the changes involved in the elaboration of tissue to which other carbohydrates, on account of their stability, were at least less readily amenable.

Mr. THISELTON DYER said that he was much mistaken if this paper did not prove to be one of the most important contributions to the study of plant metabolism of the century. The problems involved are open to two lines of attack, the botanical and the chemical: neither, in his opinion, could lead to wholly satisfactory results. It was Mr. Horace Brown's singular merit that he had been able to combine both; his conclusions may therefore be expected to be convincing both to the botanist and to the chemist.

It was not too much to say that botanists have long waited for the work which Mr. Horace Brown and his colleague are doing and have done. A good many years ago Dr. Hugo Müller had pointed out to him how far in advance in these matters the botanical results were of those which chemists had reached. And to a botanist not the least interesting feature in this paper was the frank recognition of the value, from a chemical point of view, of the classical work accomplished in this field by Sachs and Schimper. The botanical attack had for the time, however, gone as far as it could, and it awaited the chemical complement which it is now in a fair way to receive.

The primary fact of plant "assimilation" is assumed. That is an outcome of protoplasm activity, the details of which we need not discuss. The result is generally admitted to be what we may call a "proto-carbohydrate." Now this substance reveals itself in a visible and derivative form, on the one hand in cellulose and on the other in starch. The deposition of the former is the work of the general protoplasmic body of the cell; that of the latter is, as far as we know, the special function of certain specialised protoplasmic corpuscles, known as plastids. Of these, botanists now recognise three separate groups—chloroplastids, chromoplastids, and leucoplastids. The latter are identical with the amyloplasts of Schimper. We now have reason to believe that these groups may be reduced to two—the coloured and the colourless plastids; the chloroplastids in point of fact are only a particular phase of the chromoplastids. All alike possess the common property of determining the formation of "starch granules." The more we know of these bodies the more remarkable are their properties; they appear to have their own independent method of multiplication by division; it is even probable that they are bodily inherited from one plant generation to another; and both Schimper and Lankester have hinted that they may be autonomous organisms leading a commensal existence with the plant whose physiological needs they so conspicuously subserve.

Nothing is so remarkable in the general survey of plant metabolism as the repeated passage of its products from the soluble to the insoluble form, and *vice versa*. He had long been of opinion that the key to the *modus operandi* of these transformations is to be found in the action of enzymes, and had done his best to emphasise the view in an address which he gave to the British Association in 1888. But in science a merely theoretical view is of little value without a formal proof. And as regards the mode in which starch is brought into use, it appeared to him that Mr. Horace Brown had for ever set that question at rest. The difficulties raised by

Wortmann never weighed much with botanists, and Mr. Horace Brown had demolished them, as it seemed to him, for ever.

So far we were very grateful to the authors of the paper for clearing the way for us. But what follows was not, at present, free from difficulty. The botanical point of view was briefly stated by Sachs in the case of the sugar beet: starch in the leaf, glucose in the petiole, cane-sugar in the root. As he had pointed out in the *Kew Bulletin* for 1891, the facts in the sugar-cane seem to be strictly comparable. Cane-sugar the botanist looks on, therefore, as a "reserve material." He had ventured, in fact, to call "glucose" the sugar "currency" of the plant, cane-sugar its "banking reserve."

The immediate result of the diastatic transformation of starch is not glucose, but maltose. But Mr. Horace Brown had shown in his remarkable experiments on feeding barley embryos that, while they can readily convert maltose into cane-sugar, they altogether fail to do so with glucose. We may conclude, therefore, that glucose is, from the point of view of vegetable nutrition, a somewhat inert body. On the other hand, evidence is apparently wanting, that maltose plays the part in vegetable metabolism that might be expected of it. Its conversion into glucose may be perhaps accounted for by the constant presence in plant tissues of vegetable acids. But, so far, the change would seem to be positively disadvantageous. Perhaps glucose, in the botanical sense, will prove not to have a very exact chemical connotation.

That the connection between cane-sugar and starch is intimate is a conclusion to which both the chemical and the botanical evidence seems to point. And on botanical grounds this would seem to be equally true of its connection with cellulose.

It must be confessed, that the conclusion that "cane-sugar" is the first sugar to be synthesised by the assimilatory processes is one which is rather startling to the botanist. It seems hard to reconcile with its probable high chemical complexity and with the fact that, botanically, it seems to stand at the end and not at the beginning of the series of metabolic change.

A few words must be said, in conclusion, on the references made by Mr. Horace Brown to the part played by protoplasm.

"Protoplasmic continuity" is a great induction, to the establishment of which the work accomplished by Mr. Gardiner at Kew had, in great measure, contributed. He was, however, inclined to approach with caution the use Mr. Horace Brown had made of it. He was far, himself, from thinking that it can at present be relied on to explain the "rapid translocations" of metabolites. For his part, for various reasons, he had been content to think that, where a tract of tissue becomes the seat of an enzymic action (as in germination), the continuous protoplasm may act as the means of transmission of an enzyme from cell to cell, or even of some influence by which an enzyme is set free from a zymogen. But he doubted the evidence at present being sufficient to accept it as the path of the bodily transmission of a metabolite.

The resistance which living protoplasm presents to the ordinary physical processes of diffusion is an old difficulty. Invoking the continuity of protoplasm did not in his opinion materially dispose of it. But, on the other hand, it must be remembered that the cell, which is the active seat of metabolic change, is in a state of tension; and the opposition offered by protoplasm to diffusion is mitigated by the fact that it cannot be invariably regarded as a continuous membrane, but is itself, under such circumstances, frequently porous and subject to physical permeability.

He must finally relieve his mind of an idea that had often occurred to him about protoplasm as the seat of chemical changes of immense importance. In the laboratory we are accustomed to deal with organic substances as comparatively stable. Their molecular up-building or synthesis, when effected by the chemist, is generally diffi-

cult and circuitous. He thought we must accustom our minds to the fact that in the "protoplasmic field" these processes may be much more easily accomplished. Under such circumstances it appeared to him that the molecules of various substances may be subject to soliciting influences of the nature, perhaps, of solution, which, without altering their chemical identity or constitution, may make their chemical transformation far more easy to accomplish than it is by ordinary chemical means. He was not desirous of violating chemical order or law, or of claiming for protoplasm any "vitalistic" properties, but at the same time it would be absurd to shut our eyes to the unique properties that protoplasm possesses, or to refuse to admit that it may, in consequence, have the power of conditioning chemical change in a probably unique manner. At any rate he might point to the facility with which, in the field of organic nature, chemical change seems to be effected, and to the profusion of products which result from it. What nature, with the aid of protoplasm, appears able to effect with extreme facility the chemist can only follow with laborious difficulty.

No doubt it may be said that this is to introduce a new and unknown quantity into chemistry—a biological element, in fact. Why not? He could conceive that the path of chemical change in the organism may be conditioned by adaptive requirements, by natural selection in fact, and that the substances which now dominate the chemistry of plant life may have attained their prominence, not so much in obedience to unselective chemical change as to the requirements of plant life. Enzymes, for example, may, in the first place, have been mere proteid derivatives of protoplasm. But their peculiar properties of bringing about fermentative change may have rendered possible, and, therefore, stereotyped, the whole series of plant metabolism, with its singular alternation of soluble and insoluble products.

Dr. D. H. SCOTT said that since the publication of Schimper's paper of 1885, the idea that starch is not the first product of assimilation had been familiar to botanists. In fact, Sachs himself had never said that it was so, but had spoken of starch as the first *easily demonstrable* product. Botanists generally supposed, with Schimper, that glucose, or some similar sugar, is a prior product to starch. Messrs. Brown and Morris's conclusion that cane-sugar is first formed was an entirely new departure.

The paper proved that the starch formed by the chloroplasts is precisely the same thing as starch formed by leucoplasts, namely, a reserve food substance, and nothing more. So far, the chloroplast is physiologically as well as morphologically identical with an amyloplast destitute of chlorophyll. But the chloroplast has the further, quite distinct, function of forming a carbohydrate in the first instance from inorganic materials.

Messrs. Brown and Morris had shown what brilliant results might be attained when skilled chemists devoted themselves to physiological problems.

Professor GREEN, after alluding to the author's theory of the improbability of all the carbonaceous material of the plants' food passing through the starch stage, referred to the possibility that at the same time that the formation of carbohydrate was taking place there might be a coincident formation of vegetable acids, part of the increase in weight of the leaf being so accounted for; thus from formaldehyd it seemed possible to pass to formic acid, and subsequently to higher acids such as the parenchyma of the plant contains.

He asked also whether in noticing the variation of the diastatic power of the leaf at different times of the day the author's attention had been directed to a possible inhibitory effect of light upon its action. The quantity might vary as the author suggested, but it was at least possible that with a constant quantity the diastatic action might be much less in the daytime, owing to the diastase being unable to work in sunlight.

In this connection Professor Marshall Ward's experiments on the bactericidal action of certain rays were

significant, as they indicated a possibility of protoplasm being directly affected by these rays. If protoplasm itself is so interfered with, might not its enzymes also be disturbed by the same influence?

The views of Böhm and Baranetzky as to the diastase being used up in course of its activity are not in accord with the opinion of most workers on the enzymes. As Mr. Brown appeared to endorse these views to a certain extent, could he quote experiments clearing up the point? O'Sullivan's experiments on invertase (*Chem. Soc. Trans.*, Oct., 1890) pointed to a directly opposite view.

In criticising Wortmann's method of preparing his extracts, Mr. Brown had pointed out the difficulty of extracting enzymes by water. There was another solvent which, in many cases, offered great advantages, viz., a 5 per cent solution of common salt. The greater power of this as an extractive was possibly connected with the frequent association of the enzymes with globulins.

Dr. LAUDER BRUNTON observed that the paper opened up very many new lines of inquiry. It threw a light not merely on vegetable physiology and chemistry, but on the physiology of animal life, and also on that of the lowest organisms which could hardly be reckoned either as animal or vegetable. He thought that perhaps animal life in its turn might throw a light on vegetable physiology, and instanced the close resemblance that existed between the storage of glycogen in the liver of animals during digestion, with its subsequent conversion into sugar, and the temporary accumulation of starch and its subsequent removal from the leaves of plants. In the pancreas of an animal, one of the enzymes which was present in the juice of the secreting gland and also in its substance appeared to be entirely absent from the gland of fasting animals. This absence is only apparent, for the enzyme is really present, not in an active condition, but in the form of a zymogen. From this zymogen the active enzyme may be liberated by treatment with dilute chlorhydric acid and subsequent neutralisation. He was desirous to know whether any such zymogen had been found in leaves where starch was accumulating. The pancreas of animals was also remarkable in this particular, that while the gland was pouring into the intestines a juice which converts starch into sugar, it was also pouring through the lymphatics into the blood an enzyme which destroys sugar. He thought it possible that more than one enzyme might be present in the leaves of plants, and was anxious to know whether any observation had been made as to the presence of an enzyme in the plant which could decompose sugars.

(To be continued.)

PHYSICAL SOCIETY.

Ordinary Meeting, April 28th, 1893.

Prof. W. E. AYRTON, F.R.S., Past President, in the Chair.

MR. F. HARRISON was elected a member of the Society.

Adjourned discussion on "*The Viscosity of Liquids*" by Prof. J. PERRY, J. GRAHAM, and L. W. HEATH.

Prof. PERRY read a communication he had received from Prof. Maurice Fitzgerald on the subject, in which the latter discussed the corrections necessary for reducing the results obtained by circular motion to the corresponding motion in plane layers. He shows that in addition to the circular motion, the effect is complicated by radial flow, due to "centrifugal head," which causes the liquid to pass outwards near the bottom of the trough, and inwards across the edge of the suspended cylinder, with continuations along the sides of the trough and cylinder. Taking this motion into account, the formula—

$$v = Ar^{1+\mu} + \frac{B}{r}$$

is deduced, where v is the velocity, μ the viscosity, A and B arbitrary constants, and c a constant depending on the radial flow. When $c=0$ the formula reduces to equation (5) of the paper, whilst if $c=-2\mu$ it becomes—

$$v = \frac{C}{r}.$$

The subject of critical velocities in non-turbulent motion is referred to, and some probable effects of the anomalous variations of density and viscosity of sperm-oil noticed by the authors of the paper are pointed out.

Prof. PERRY, in further reply to Prof. Osborne Reynolds' comments, said he understood Prof. Reynolds to have proved that friction was proportional to velocity when the motion was steady. Experiments he (Prof. Perry) had made with discs of iron and glass in revolving mercury seemed to show that this was not the case. On replacing the mercury by sperm-oil he found that up to a certain speed friction was strictly proportional to velocity, whilst above that speed friction varied as $v^{1.25}$. Coloured streaks in the liquid remained unbroken even at the highest speeds. He therefore concluded that continuity of the streaks was not necessarily accompanied by a linear law of friction.

Mr. E. C. RIMINGTON read a paper on "*Luminous Discharges in Electrodeless Vacuum-Tubes.*"

The luminous rings produced in exhausted bulbs and tubes by discharging Leyden jars through coils surrounding them had, he said, been attributed by Mr. Tesla (*Electrical Engineer* of New York, July 1, 1891), to the electrostatic action of the surrounding wire rather than to the rapidly varying magnetic induction through the rarefied gas. The present paper describes several experiments bearing on this point, which leads the author to conclude that varying magnetic induction is the chief cause of the luminous rings. They also show that a superposed electrostatic field greatly assists the production of the luminosity. Most of the experiments described were performed before the meeting, some of the effects being particularly brilliant. In one experiment an exhausted bulb was placed within a coil connecting the outside coatings of two Leyden jars, and placed between two metal plates which could be connected at will with the outside of either jar. The spark gap between the inner coatings was then arranged so that no luminosity was seen in the bulb. On connecting one or both the metal plates with the jars in such a way as to increase the electrostatic field through the bulb, bright rings immediately appeared. An electrostatic field produced by a small induction coil connected to a piece of tin foil on the bulb caused the rings to form at irregular intervals when the discharge of the jars and coil happened to be properly timed. In another experiment two loops of wire in series were used, and when put on the bulb in such a way as to produce a large magnetic effect but small electrostatic field, bright rings appeared; but if the magnetic effects of the coils opposed each other, whilst the electrostatic field was increased, no rings were seen. The subject is treated mathematically at some length in the paper, the times at which the maximum values of the current—the potential difference between the outsides of the jars and the rate of change of current—occur, as well as the values of their successive maxima being determined. The influence of "size of jars" is next considered, and the time integral of rate of change of current on which the effect on the eye depends expressed as a geometrical series. Taking an approximation, the author shows that the time integral is roughly proportional to the fourth root of the capacity. Large jars are therefore theoretically only slightly better than small ones, and this agrees with observation.

On the subject of "apparently unclosed discharges," such as are seen when discharges pass through a coarse spiral wound on an exhausted tube, the author said he had observed that the discharges were really closed, but the return part was much diffused and of feeble intensity.

Experiments were exhibited showing that under some circumstances an exhausted bulb acted like a closed metallic circuit, whilst under other conditions dissimilar effects were produced. Another experiment was shown in which a faint luminous ring produced by a single turn of insulated wire round a bulb, was apparently repelled on touching the wire with the finger. The author also showed that fan-shaped luminosities could be produced by rotating an exhausted tube in the electrostatic field produced by a charged ebonite or glass rod.

Dr. SUMPNER, speaking of the apparently unclosed discharges, pointed out that they might be closed through the wire forming the primary circuit in the same way as a coil of a transformer might be arranged to act, partly as primary and partly as secondary.

Mr. A. P. TROTTER, after referring to Dr. Bottomley's researches, said it was important in discussing such experiments to distinguish between electrostatic and electromagnetic effects. In Mr. Campbell Swinton's experiments the luminosity always appeared to get as far away from the wire as possible, and to be at right angles to it; whereas in Mr. Rimington's the luminous portions were close to the wire. With a view to puzzling the discharge in Mr. Swinton's tubes, he had made a right angled bend in the spiral surrounding the tube, the result of which was to make the luminosity discontinuous, one end of the break being bifurcated. In all Mr. Swinton's experiments brush discharges surrounded the wire.

Prof. S. P. THOMPSON thought an electrostatic field would aid a discharge even if its direction was not the same as the E.M.F. due to varying magnetic induction. Planté had found that vacuum-tubes through which 800 cells were insufficient to produce a discharge, immediately allowed a discharge to pass when a rubbed ebonite rod was brought within about ten feet distance. This effect was found to be independent of the direction of the disturbing field. Analogous effects had also been observed by Prof. Schuster, and described in his Bakerian Lecture.

Mr. E. W. SMITH regarded the stresses set up in the medium as cumulative, a very slight cause acting on a substance already strained nearly to breaking-point being sufficient to cause breakdown.

Mr. BLAKESLEY inquired if the effects were the same if the induction-coil used in one of the experiments was replaced by an electric machine, and whether the direction of the field so produced influenced the result.

Mr. W. R. PIDGEON said closed circuits were necessary; he had found it very difficult to produce discharges in tubes unless the ends of the primary wire were brought together.

In his reply, Mr. RIMINGTON said each turn of the luminous spiral formed a complete circuit of itself. The phenomena observed by Mr. Campbell Swinton were quite different to those he had shown and due to different causes. Mr. Swinton's spirals were reversed, and were due to phosphorescence of the glass.

NOTICES OF BOOKS.

A Manual of Dyeing. For the Use of Practical Dyers, Manufacturers, Students, and all interested in the Art of Dyeing. By EDMUND KNECHT, Ph.D., F.I.C., Head of Chemistry and Dyeing Department of the Municipal Technical School, Manchester; Editor of the *Journal of the Society of Dyers and Colourists*; CHRISTOPHER RAWSON, F.I.C., F.C.S., late Head of the Chemistry and Dyeing Department of the Technical College, Bradford; Member of Council of the Society of Dyers and Colourists; and RICHARD LOEWENTHAL, Ph.D. With numerous Illustrations and Specimens of Dyed Fabrics. Two vols., 8vo., pp. 907, and a Third vol. of Dyed Patterns. London: Charles Griffin and Co., Lim.

Of all the departments of chemical industry none have probably undergone a change so complete as the tinctorial

arts. It is not too much to say that an experienced dyer—at once practical and theoretical—of the middle of the present century would be no little puzzled could he take up these volumes and glance through their contents. He would not merely encounter a host of new dye-wares and miss his old familiar friends, or at least find their relative importance greatly diminished, but he would encounter new principles. In place of the long lists of recipes he would find his attention called to the underlying conditions. Here it is that the dyer of the old school often went astray. As long as he had the same water, the same wares, and the same growth, say, of wool year by year, he could produce excellent work; but place him amidst new conditions and he felt lost. But the dyer of the new school, if properly trained, knows how to accommodate himself to varying circumstances.

The rival theories of the process of dyeing are duly expounded. The balance of evidence seems now to turn more and more in favour of the chemical theory. The chemical character of cellulose is carefully studied. A curious fact is the obstinacy with which Mercer's great invention has been and is still disregarded, although a French company, as we are told, offered him the sum of £40,000 for his patent rights.

As the average proportion of moisture in wool is no less than 18.25 per cent, it is interesting to learn that, following the example of the chief industrial countries abroad, a "conditioning house" has been established at Bradford in which the moisture of wools sold is officially tested.

The moisture in manufactured woollen goods, e.g., blankets, is not to our knowledge under any official control. Hygroscopic substances are or have been employed by certain manufacturers for the purpose of increasing their weight.

Mention is here duly made of some of the injurious effects of the sulphur naturally present in wool. The comparative behaviour of wool and of silk with reagents is very fully and ably explained.

The authors judiciously advise that in localities where the ordinary water supply is hard, or otherwise impure, the owners of dye-works might with advantage pay more attention to the collection and storage of rain-water. The evils of hard and especially of ferruginous water are fully described.

It is stated that only one firm in England (Messrs. Ainsworth and Co., of Bolton) are using the Mather-Thompson bleaching-process, notwithstanding its demonstrated advantages. The electrolytic bleaching-process is not described.

In wool-bleaching, the use of stale urine (lant) is said to have been almost entirely superseded in England. Among the by-products of wool-washing, the potassium carbonate is said to be more valuable than the fatty matters. But in any case the suint and the fat from the soaps used in washing and milling must be recovered to avoid the pollution of the streams. The use of volatile liquids for wool-washing has not yet become general.

In bleaching wool and woollen goods sodium bisulphite and liquefied sulphur dioxide are coming into use, gaseous sulphurous acid (the old stoving process) being very injurious to the workmen. The use of hydrogen peroxide is restricted by its high price. It is a curious fact that for silk-bleaching neither sodium bisulphite nor liquefied sulphurous acid have proved satisfactory.

The preparation and properties of "alizarin oil" is discussed at some length and presents some unsettled points.

It is somewhat remarkable that in the very elaborate section on the tannins, though their use in "weighting" or "loading" silks is mentioned, yet the plainly fraudulent character of this process does not meet with a word of condemnation.

The section on mordants is fully on a level with present practice. Since the general introduction of the coal-tar colours, the importance of the tin mordants has greatly

declined, and many preparations once highly valued have now little more than a historical importance. On the contrary, the antimonial mordants are coming more into use.

The recent enactment for the addition of coal-tar naphtha to methylated spirit,—thereby spoiling it for a number of purposes—is mentioned without criticism. If there was danger lest the spirit might be applied to non-technical uses, why was not a minute addition of Dippel's animal oil employed, as is the case in Germany?

In Part VI., which treats of the natural colouring-matters, we find the statement that in England the old law prohibiting the use of indigo has never been repealed! It is, of course, practically obsolete; but it might at any time be revived by an evil disposed person.

It is interesting to find that the part played in indigo-dyeing by a micro organism, *Desmobacterium hydrogeniferum*, is here fully recognised.

Is it not possible that improvements may be effected, e.g., in the production of the weed-colours by the use of pure microbial cultures?

We hope to resume our notice of this most valuable work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 17, April 24, 1893.

New Researches on Micro-Organisms. Fixers of Nitrogen.—M. Berthelot.—The author's experiments prove that there exist microbes of very different species, free from chlorophyll, and capable of fixing nitrogen, especially certain bacteria of the soil. It is seen that the nutrition of these plants does not appear capable of being maintained by the carbon and hydrogen resulting from the decomposition of the atmospheric CO₂ and H₂O. It is correlative with the destruction of certain hydrocarbons such as sugar or tartaric acid, which in some way act as foods for the bacteria and (other?) micro-organisms. For these beings to fix nitrogen it is necessary that they must find suitable nutriment in the medium where they live. It even appears necessary that these substances must contain some little nitrogenous matter in order to give the lower organisms the minimum of vitality necessary for the absorption of free nitrogen. But if these nitrogenous principles are too abundant the bacterium subsists by preference at their expense.

Study of Solutions of Ferric Chloride and Oxalate. Distribution of Ferric Oxide between Hydrochloric Acid and Oxalic Acid.—George Lemaine.—A thermochemical paper, which requires the accompanying diagram.

Some Derivatives of Licareol.—Ph. Barbier.—It results from the author's experiments that licareol is a primary alcohol, which may be represented by the formula C₉H₁₅CH₂OH. The residue C₉H₁₅ admits of two ethylenic connections. Hence licareol is an alcohol with an open chain.

Constitution of Gallic Blue or Tannin Indigo.—P. Cazeneuve.—This product is the anilide of gallic acid obtained by the action of nitrosodimethylaniline upon the crystalline product, resulting from the action of aniline upon tannin.

On the Chloramines.—A. Berg.—Methylchloramine is produced by the action of sodium hypochlorite upon methylamine hydrochlorate. It is a colourless, very volatile liquid of an exceedingly pungent irritating odour. It is rather soluble in water, which dissolves about the

tenth of its volume. Dimethylchloramine is obtained in the same manner. It is a liquid almost colourless and of a pungent smell. It boils at 46° under a pressure of 765 m.m. Its density at 0° is 0.986. Water dissolves an eighth of its volume.

Bornylates of Borneol.—J. Minguin.—The author examines the influence of bromal upon the camphols.

He has experimented upon dextro-borneol α , levo-borneol α , borneol β or levo-isocamphol, borneol β or dextro-isocamphol, and has given a table of their physical constants.

Qualitative and Quantitative Analysis of Form-aldehyd.—A. Trillat.—This paper will be inserted in full.

Journal für Praktische Chemie.

New Series, Vol. xlv., Parts 20, 21, and 22.

Action of Gaseous Hydrochloric and Hydrochloric Acids upon Liquid α -Dichlorcyanethyl.—Dr. J. Troeger.—For this paper we must refer to the original.

Researches on Alloisomerism.—Arthur Michael.—These researches comprise three papers: a memoir by A. Michael and G. Tissot on the addition of chlorine to polybasic, non-saturated fatty acids; a comparison of the experimental results with the theoretical deductions from the hypotheses of Le Bel, Van't Hoff, and Wislicenus; a critique on the hypothesis of Van't Hoff in its application to the mutual relations of saturated and non-saturated fatty acids. In sulphured wines the sulphurous acid exists in part free and in part as sulphuro-aldehydic acid. Both forms of sulphurous acid can be directly titrated in the manner directed. In wine there are no volatile constituents capable of being oxidised by iodine. The purification of barium sulphate with hydrochloric acid gives occasion to serious errors in the determination of sulphuric acid. The determination is accurate if the barium sulphate is purified with bromine-water and hydrochloric acid. The strictly analytical portions of this paper will be given *in extenso*.

Knowledge of the Mixed Fatty Aromatic Ketones.—Ad. Claus.—Not adapted for useful abstraction.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 6.

Improved Apparatus for Decomposition and Absorption.—W. Thörner (*Zeit. Angewandte Chemie*).—The decomposition flask, which, according to circumstances, may hold from 200 to 1000 c.c., has a neck 350 m.m. long and 16 m.m. wide, connected by means of a caoutchouc stopper with a suitable light glass jacket and secured to a support. Into this jacket opens an influx and efflux tube for water, so that the neck of the flask forms a reflux-code. The mouth of the flask is closed with a caoutchouc stopper with two perforations. Into one of these fits a small elbow-tube bent at right angles in direct connection with the absorption apparatus. The other end is fitted with a tube funnel with a cock, its lower end reaching almost to the bottom of the flask. Below the cock is a short lateral tube for the introduction of a purified air, carbon dioxide, hydrogen, &c. For determining sulphur in iron, in antimony sulphide, iron sulphide, &c., which are decomposed by means of hydrochloric acid, and the hydrogen sulphide evolved is received in an oxidising absorbent, so that barium sulphate may be ultimately weighed, Thörner connects the decomposition flask with a two globe absorption apparatus. It consists of a glass tube about 12 m.m. wide and 350 to 400 m.m. long, turned slightly upwards and rounded at each end, with a bulb turning upwards. The outer bulb contains 100 and the inner 150 c.c., so that a reflux of the liquid is impossible. The gas has to pass a layer of liquid of about 350 m.m. and to overcome only a slight pressure, a column of water

of 30 m.m. The apparatus, besides the purpose above named, can be used for the absorption of ammonia in the examination of water, and in determinations of nitrogen by the Kjeldahl method, the ammonia being driven out by a current of air. The apparatus may also be used for determining CO_2 in minerals and in beer, if the necessary protective tubes are introduced. The carbonic acid is absorbed in a potassa apparatus.

A Syphon for Drawing off Hot Liquids.—J. Ch. Essner.—From the *Bulletin de la Société Chimique de Paris*.

Detection of Hyponitric Acid in Sulphuric Acid.—J. H. Wilson.—From the *Pharm. Journal*.

MISCELLANEOUS.

The Royal Society.—The following is a list of the selected candidates:—Prof. William Burnside, M.A., Prof. Wyndham R. Dunstan, M.A., William Ellis, F.R.A.S., Prof. J. Cossar Ewart, M.D., Prof. William Tennant Gairdner, M.D., Ernest William Hobson, D.Sc., Sir Henry Hoyle Howorth, K.C.I.E., Edwin Tulley Newton, F.G.S., Charles Scott Sherrington, M.D., Edward C. Stirling, M.D., John Isaac Thornycroft, M.Inst.C.E., Prof. James William H. Traill, M.D., Alfred Russel Wallace, LL.D., Prof. Arthur Mason Worthington, M.A., Prof. Sydney Young, D.Sc.

MEETINGS FOR THE WEEK.

- MONDAY, 15th.—Society of Arts, 8. "Mosaic—its History and Practice," by C. Harrison Townsend. (Cantor Lectures).
TUESDAY, 16th.—Institute of Civil Engineers, 8.
Pathological, 8.30. (Anniversary).
Royal Institution, 3. "Modern Society in China," by Prof. R. K. Douglas.
Society of Arts, 8. "Aspects of Federation," by W. B. Perceval.
WEDNESDAY, 17th.—Society of Arts, 8. "Composite Heliography," by F. E. Ives.
Meteorological, 7.
Microscopical, 8.
Pharmaceutical, 11 a.m. (Anniversary).
THURSDAY, 18th.—Royal, 4.30.
Royal Institution, 3. "The Geographical Distribution of Birds," by R. Bowdler Sharpe, LL.D.
Society of Arts, 8. "Agrarian Legislation for the Deccan, and its Results," by Sir Raymond West.
Chemical, 8. "Observations on the Production of Ozone during Electric Discharge through Oxygen," by W. A. Shenstone and M. Priest.
"The Relative Strengths or Avidities of some Weak Acids," by Dr. Shields. "The Boiling-points of Homologous Compounds," Part I., by Dr. James Walker.
FRIDAY, 19th.—Royal Institution, 9. "Poetry and Pessimism," by Alfred Austin.
Quekett Club, 8.
SATURDAY, 20th.—Royal Institution, 3. "Johnson and Wesley," by Henry Craik, LL.D.

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TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 1500 tons of **MANGANATE OF SODA.**

The Specification, Form of Tender, and other particulars may be obtained on application to the Engineer of the Council, at the County Hall, Spring Gardens, S.W., until Monday, the 5th June, 1893. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., and must be endorsed "Tender for Manganate of Soda," and be sent in not later than 10 o'clock on Tuesday morning, the 6th June, 1893.

Persons tendering will be required to declare in their tenders that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
10th May, 1893.

TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 5000 tons of **PROTO-SULPHATE OF IRON.**

The Specification, Form of Tender, and other particulars may be obtained on application to the Engineer of the Council, at the County Hall, Spring Gardens, S.W., until Monday, the 5th June, 1893. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., and must be endorsed "Tender for Proto-Sulphate of Iron," and be sent in not later than 10 o'clock on Tuesday morning, the 6th June, 1893.

Persons tendering will be required to declare in their tenders that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
10th May, 1893.

TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 1700 tons of **SULPHURIC ACID.**

The Specification, Form of Tender, and other particulars may be obtained on application to the Engineer of the Council, at the County Hall, Spring Gardens, S.W., until Monday, the 5th June, 1893. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., and must be endorsed "Tender for Sulphuric Acid," and be sent in not later than 10 o'clock on Tuesday morning, the 6th June, 1893.

Persons tendering will be required to declare in their tenders that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
10th May, 1893.

TO LIME MERCHANTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 20,000 tons of **LIME**, delivery to commence in June next.

Persons tendering will be required to declare in their tenders that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Engineer of the Council, at the County Hall, Spring Gardens, S.W., until Monday, the 5th June, 1893.

Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., and must be endorsed "Tender for Lime," and be sent in not later than 10 o'clock on Tuesday morning, the 6th June, 1893.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
10th May, 1893.

J. S. MERRY AND CO.,
ASSAYERS AND ANALYTICAL CHEMISTS,
SWANSEA.

**FLETCHER'S
THERMO-HYDROMETER.**

It is scarcely necessary to insist upon the vital importance of noting the temperature of a liquid when determining its specific gravity. Hitherto it has been necessary to employ separate instruments for the two observations, such combinations as were available being clumsy, slow, and untrustworthy. In **FLETCHER'S THERMO-HYDROMETER** the bulb of the Thermometer is BLOWN IN ONE PIECE WITH THE BULB OF THE HYDROMETER, and comes into direct contact with the liquid to be tested, thus ensuring the utmost sensitiveness. The Thermometer and Hydrometer scales being in juxtaposition on the same stem, A READING OF EACH CAN BE TAKEN SIMULTANEOUSLY.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1747.

ON THE ABSORPTION-SPECTRA OF SOME COMPOUNDS OF CHROMIUM.*

By W. LAPRAIK, Ph.D., F.I.C.

(Continued from p. 221).

Absorption Spectra produced by the Solution of Chromium Hydroxide in Various Organic Acids.

It was then thought to be of interest to examine the absorption spectrum given by solution of chromium hydroxide in various other organic acids, for the purpose of seeing how the spectroscopic relations differed from the known differences of constitution of the acids employed. The following acids were chosen for this purpose:—Formic, acetic, propionic, butyric, isobutyric, valerianic, heptylic, monochloroacetic, dichloroacetic, trichloroacetic, tribromoacetic, glycollic, lactic, trichlorolactic, malic, tartaric, citric, and isethionic acids.

Formic Acid (13).—This acid easily dissolves freshly precipitated chromium hydroxide. The solution has a greenish blue colour by daylight, but in thick layers by lamplight it is red, in thinner layers it is green. The absorption spectrum (13) is made up of two dark bands, 721–714 and 674–666 respectively: also of two fainter and thinner bands lying between them at 704 and 689 respectively. Then the broad absorption which begins with a shadow at 650 becomes dark at 611 and ends at 544, and beyond, continuous absorption from 470.

Several different specimens of chromium hydroxide were used, but the resulting absorption spectra of the various solutions did not differ from the above. In some experiments the solution was digested with an excess of chromium hydroxide; in others an excess of acid was used. Heat also had no effect in altering the position of the bands, but the whole spectrum then became obscured by general absorption.

Acetic Acid (13a).—This acid also easily dissolves chromium hydroxide. The solution is green by daylight; by lamplight in thick layers it is red, but in thin layers it is green. The solution gave an absorption spectrum which could not be distinguished from that given by the formic acid solution. The absorption spectra given by the two solutions containing formic and acetic acids were superposed by means of a right-angled prism, but no difference in the position of the bands could be observed. Experience showed that minute differences in the positions of narrow bands could best be made evident by making the cross-wires of the telescope coincident with the centre of the band, and fixing the telescope by a clamp to the stand; then, without removing the eye from the eyepiece, placing the solution to be compared in front of the slit, and noting if the centre of the band under examination was coincident with the cross-wires of the telescope. But even by this method no difference could be detected between the two solutions. Thinking that my own spectroscope had not a sufficient dispersion I had placed at my disposal by the kindness of Professor Wiedemann a more powerful instrument. I used in the first instance two prisms, the source of illumination being first the electric light, and secondly sunlight reflected from a heliostat. The dispersion was too great to admit of the bands being distinguished. A very finely ruled grating was now substituted; the source of light being both sunlight and electric light, no change could be detected in the position of the bands in the two solutions under examination.

Propionic Acid (14).—This was the next acid used as a solvent for chromium hydroxide. The colour of the solution was the same as in the case of formic or acetic acids. The absorption-spectrum had the same number of bands, which were of the same character as in the cases previously mentioned. On comparison of this absorption-spectrum with that given by the formic acid solution, it was found that the darker bands which could be more easily measured were slightly moved in the direction of the red part of the spectrum. The measurements (14) for the two dark bands are 729–717 and 676–668. The faint band was at 707, while the other faint band, which is more difficult to measure, appears at 689. That is the same as in formic acid, but this is, I believe, accidental for the reason stated above, and it is my impression that the whole spectrum is moved by the same amount nearer the red end of the spectrum.

Butyric Acid (15).—This was the next acid used as a solvent for chromium hydroxide. The solution was greenish-blue by daylight, and red or green, according to the thickness of solution examined, by lamplight. It is observable that the more complex acids of this series dissolve less of chromium hydroxide, and with much greater difficulty. The solution obtained gave an absorption-spectrum identical with that given by propionic acid.

Isobutyric Acid (15a).—This acid does not dissolve chromium hydroxide so readily as butyric acid, but after a time a solution was obtained sufficiently strong. It had a green colour both by daylight and lamplight. The absorption spectrum of this solution was carefully compared with that given by butyric acid; but it was found that the absorption-spectrum in the case of isobutyric acid was identical with that produced by butyric acid.

Valerianic Acid (15b).—This acid dissolves chromium hydroxide with great difficulty, but after some time a solution was obtained for examination. The colour of the solution was green both by daylight and lamplight, and gives an absorption-spectrum analogous to the other acids of the series, but the bands are much less distinct than in the case of the acids previously mentioned. I carefully compared this absorption spectrum with that given by formic, acetic, and propionic acids, and I found that there was a slight but distinct movement of all the bands towards the red end of the spectrum, which was more perceptible in the next acid examined.

Heptylic Acid (16).—This acid dissolved the chromium hydroxide with difficulty, but after prolonged digestion sufficient was obtained in solution to give an absorption-spectrum with a thickness of 2.5 c.m. The solution was green by daylight and red by lamplight. Its absorption-spectrum was identical—as far as the number of absorption-bands and their relative intensities are concerned—with that given by the other acids of the series; but in the case of the heptylic acid solution the absorption-bands were distinctly moved further to the red end of the spectrum than was the case in any of the other acids previously mentioned.

I confirmed this result by using another spectroscope of greater dispersion, which Dr. Acworth was good enough to lend me, and which he has described.* I avail myself of this opportunity of thanking him for the use of the same.

The measurements made on my own instrument of the heptylic acid solution are as follows (16). The two dark bands are from 732–719 and 681–674 respectively. The two fainter bands are 708 and 695. Then the broad absorption from 650–544, and continuous absorption from 480. The fainter bands at 708 and 695 are not nearly so well marked as the two other darker bands. This remark applies also to all the acids examined belonging to this series; therefore there is considerable difficulty in

* Journ. für Prakt. Chemie, xlvii., 305 (1893).

* J. J. Acworth, "Beziehung Zwischen Absorption und Empfindlichkeit Sensibilisierter Platten" (1890).

measuring them, especially in this case, as one requires to work with a slit of small aperture in order to see them at all. In the case of such faint absorption-bands, repeated measurements were made till concordant numbers were obtained.

It has now been shown that when chromium hydroxide is dissolved in the fatty acids previously mentioned, absorption-spectra are produced which are quite analogous in structure; and we have here another instance of the movement of the absorption-bands towards the less refrangible end of the spectrum as the molecular complexity of the body examined increases. But the known difference of the structure of the isobutyric acid molecule from that of the butyric acid molecule does not appear to alter the position of the absorption-bands.

It is further observable that the higher acids of the fatty acid series give—when chromium hydroxide is dissolved in them—bands less distinct and less dark than is given by the lower acids of the same series. The broad absorption in the green part of the spectrum of these chromium compounds is usually so indefinite at the edges that it is impossible to say if it also moves with the other bands, but there is reason to believe that it does.

It is remarkable that an acid so different in constitution, and in almost every other respect to the fatty acids as succinic acid is, should, when chromium hydroxide is dissolved in it, give an absorption-spectrum practically identical with that given by propionic or butyric acids when similarly treated. Yet it is so, for I repeated the experiment with three different specimens of chromium hydroxide without any different result; nor was I able to observe that any decomposition of the acid occurred. At present I am not able to give any explanation of this remarkable spectroscopic analogy.

To be continued).

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

FIRST PAPER: THE ANALYSIS OF BARIC BROMIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 223.)

Balance and Weights.

THE balance and weights were identical with those used in the latter part of the investigation upon copper (*Proc. Amer. Acad. Arts and Sciences*, xxvi., p. 242), hence a further description of them is unnecessary. The weights were gently and carefully rubbed, and again standardised with reference to each other; a proceeding which yielded values essentially identical with the two previous standardisations. The first ten-gramme weight was also compared from time to time with the platinum weight which had been carefully standardised in Washington (*loc. cit.*) in order to test its constancy.

		True Grammes.
Oct. 18, 1891	Ten-gramme weight	= 10.00023
May 16, 1892	"	= 10.00023
Nov. 1, 1892	"	= 10.00022
Nov. 2, 1892	"	= 10.00020

* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

The second ten-gramme weight, which was much less used, remained quite constant in value.

Throughout the present investigation the method of weighing by tares was universally adopted. A vessel to be weighed was placed upon the left hand scale pan, balanced with common gilded weights, and then replaced by a similar vessel which weighed a few milligrams less. The exact amount of this extra tare having been determined with the rider, the counterpoise was replaced by the original vessel and the rider removed, in order to determine if the centre point had changed. When only a slight change had taken place, the reading for the counterpoise was compared with the mean of the two readings for the original vessel. In the rare cases when the change exceeded the equivalent of the thirtieth of a milligram, the vessels were alternately substituted for each other until constancy was reached. A substance to be weighed was of course placed in such a tared vessel, and after substitution the deficiency of the counterpoise was made up with standard weights. The difference between the tares on the left hand scale pan indicated the observed weight in air of the substance taken. It was found convenient to tabulate the results in the form given in Table below.

The lowest right hand figure represents the true weight of the substance taken, if the Sartorius ten-gramme weight is taken as the standard. Reduced to the Washington standard the value becomes 1.80934; but this last correction is in no case applied in the work which follows.

The method used in the case of hygroscopic substances, and most other precautions, are given at length in the paper already quoted. In weighing a crystallised salt it was usually necessary to weigh the crucible while filled with ordinary moist air, hence the counterpoise crucible was exposed to the same conditions.

During the latter part of the investigation the balance was kept in a small room built entirely inside of the main laboratory. The absence of outside windows in the small room caused a notable absence of air currents and rapid changes of temperature, while its glass walls supplied plenty of light.

It is almost needless to state that, while the weights of the apparatus were not reduced to the vacuum standard, —on account of the method of weighing, which rendered such reduction unnecessary,—the weight of every substance used was corrected in the manner shown above for the difference between the weight of air displaced by it and that displaced by the corresponding brass weights. Where the specific gravity of the substance was not already accurately known, it was carefully determined for this purpose.

The Spectroscopic Detection of Calcium and Strontium in the Presence of Barium.

In the course of the search for a typical barium salt it became important to determine how small an amount of calcium and strontium could be detected in the presence of large amounts of barium. The most sensitive method is naturally the spectroscopic one, but no literature giving the degree of sensibility seemed to be at hand.

The first phase of the problem to be investigated was the determination of the amount of calcium and strontium which could be detected in the absence of barium. Hence a standard solution of calcium and strontium was prepared containing 0.8 m.grm. of each metal to the c.c. This solution was successively diluted and tested by means of a well made single prism spectroscope with an

	Common Weights; Rt. hand pan. Grms.	Tare: Standard Wts. L. hand pan. Grms.	Cor. to Standard Weights. M.grms.	Corrected Standard Weights. Grms.	Correction to Vacuum. M.grms.	True Wt. of Substance taken. Grms.
Weight of crucible + substance	22.0890	1.80986	-0.05	1.80981		
Weight of crucible alone	20.2797	0.00081	0.00	0.00081		
Wt. of substance, cryst. baric bromide	1.8093	1.80905		1.80900	+0.30	1.80930

adjustable slit. A drop of the solution was supported upon a coil of wire containing 0.018 c.c., similar to that suggested by Truchot (*Comp. Rend.*, lxxviii., 1022) and so ably used by Gooch and Hart (*American Journal of Science*, [3], xlii., 448); the writer is much indebted to this paper for valuable hints. No attempt at quantitative analysis was made, the present problem being merely the determination of the limit of visibility.

Results.

Dilution.		Weight of Ca and Sr vapourised.	Observations.
Solution :	Water.	M.grms.	
I :	0	0.014	Brilliant.
I :	5	0.003	"
I :	10	0.0014	Very plainly visible.
I :	20	0.0007	" " "
I :	40	0.0004	Plainly visible.
I :	100	0.00014	Both visible.
I :	200	0.00007	Both scarcely visible.
I :	400	0.00004	Both invisible.

Hence seven hundred-thousandths of a m.grm. is about the limit of visibility under these conditions. It is remarkable that this result should be essentially identical with Bunsen's result obtained by a different method (compare Vogel's "Spectralanalyse irdischer Stoffe," 1877, pp. 92, 94).

It has long been known (compare Vogel's "Spectralanalyse irdischer Stoffe," 1877, p. 99) that the best method for detecting small quantities of strontium and calcium in the presence of barium is to evaporate the solution of the chlorides to small bulk, precipitate most of the baric chloride by means of alcohol, and test the filtrate. From this filtrate, by means of two or three repetitions of the fractionation with alcohol, it is possible to eliminate nearly all the barium. It is evident, on the other hand, that if the precipitate is dissolved and re-precipitated several times, all the calcium and strontium must go into the mother liquors. This is one of the most rapid methods of obtaining pure baric chloride; it served for the preparation of the material used in the succeeding experiments.

In the first experiment half a m.grm. of calcium was added to the solution of three grms. of very pure baric chloride. Upon the usual fractional treatment a most brilliant calcium spectrum was obtained from the mother liquor. One-fifth of a m.grm. of calcium in another experiment gave similar results. For a third experiment one-fiftieth of a m.grm. each of calcium and strontium was added to five grms. of crystallised baric chloride. The mother liquor from the first precipitation by alcohol was evaporated to dryness and extracted with alcohol. Calcium was very evident in the extract, but no trace of strontium. The reason for the apparent absence of the latter metal is to be found in the fact that the mother liquor was evaporated to dryness. To prove this, the same amount of materials were fractionally precipitated three times, and a very evident strontium spectrum was given by the last mother liquor. In the fifth trial, only one two-hundredth of a m.grm. of strontium was used. Upon three fractionations no strontium could be detected, but upon dissolving and re-precipitating each of the precipitates once more a faint test for the metal was found in the final mother liquor. This is evidently about the limit so far as strontium is concerned. Calcium may be detected when it is present in quantities much less than the two-hundredth of a m.grm., because of the ready solubility of its chloride in alcohol. The baric chloride used gave no trace of the calcium or strontium lines after most careful fractionation.*

From these experiments it may be concluded that when a baric salt shows no trace of the allied metals upon the

treatment just described, it does not contain a weighable amount of them. Nevertheless, in the work which follows, the purification was usually continued long after the visible traces of strontium and calcium had been eliminated.

(To be continued).

INSTRUCTIONS FOR THE EXAMINATION AND JUDICIAL DECISION ON PORTIONS OF ANIMAL ORGANISMS INTENDED FOR HUMAN FOODS.*

By WILHELM EBER.

(Concluded from p. 222).

If fumes were present the gaseous column becomes clear in five to ten minutes, and the glass after careful shaking is ready for another test. Such a glass may serve for many hundred trials without requiring a renewal of the liquid. A renewal is necessary as soon as the inner sides of the glass have become dirtied, or parts of the specimen have fallen into the liquid, or the reagent is spoiled. The last is the case as soon as a drop of pure water placed on the glass produces a mist, or ammonia no longer forms a cloud.

(e) The reaction is ascertained by pressing a narrow slip of moistened litmus paper upon the specimen by means of a clean knife (not the fingers, which have often an acid reaction). After ten minutes the papers are lifted off the object, laid upon white paper, and compared with another slip of the original litmus paper, also moistened.

3. Condition Internally.

(a) The surface is washed clean from any adhering deposit.

(b) A deep section is made extending at least to the middle of the object, or the interior is laid bare in some other manner.

(c) Colour and general appearance of the recent sections (escape of gas-bubbles?).

(d) The odour is ascertained on an unobjectionable portion of the specimen which has not come in contact with any other portion.

(e) The reaction is determined with litmus paper.

(f) Ammonia test for putridity.

(g) Consistence.

(h) Change of freshly-cut surfaces on exposure to air.

(i) Boiling test. It is, in general, applied only to salted or pickled meat in order to ascertain if such meat is thoroughly pickled (permanence of red colour after boiling, firm consistence), and whether odours not perceptible in the cold are evolved on heating.

(j) Test for hydrogen sulphide.

The diagnosis may indicate:—

1. Simple acidity. Faintly acid or amphoteric reaction, specific odour of the animal species, no ammoniacal fumes.

2. Acid fermentation. Strongly acid reaction, no ammoniacal fumes.

3. Putridity. Reaction alkaline, amphoteric, or neutral. (Traces of grey mist which disappear in passing from the glass rod to the level of the liquid are unmeaning). The specimen is putrid if the decomposition indicated by the ammonia test has reached such a height that the portions affected cannot be separated from the remainder.

4. Mixed processes. Reaction acid, ammoniacal fumes. In practice such processes are pronounced incipient putrefaction.

5. Decompositions of indefinite character. No action upon litmus paper; merely changes of colour, (e.g., luminosity in the dark) in odour and consistence. Includes foods of inferior value.

* From the *Zeit. Anal. Chemie*.

* A trace of sodium was always found in even the purest specimens. It is probable that this trace was derived from the air during the course of fractional treatment necessary to eliminate the barium.

ON A NEW METHOD FOR THE BACTERIOLOGICAL EXAMINATION OF WATER.

By A. B. GRIFFITHS, Ph.D., F.R.S.E., F.C.S., &c.

Introduction.

THE study of microbes is not only of the greatest value to the pathologist and physician, but concerns the chemist, sanitarian, brewer, manufacturer, and agriculturist; in fact, it concerns all, for there is not a moment of our lives in which we are not in contact with "the unseen mist of organic forms." It may be said that microbes are omnipresent,—that they are always present in water, air, and soil. Their numbers vary, however, with the nature of the water, air, and soil; the time of the year and various climatic conditions also influence their rate of increase.

Although in the present paper we deal with the microbial examination of water, it may be stated that many microbes present in water are also found in the air and soil. The state of the atmosphere influences to a certain extent the number of microbes present in water. For instance, after a considerable amount of rain the atmosphere contains fewer microbes than it does in fine weather; but, on the other hand, rivers and natural waters generally contain (as a rule) larger numbers of microbes in wet than in fine weather. Then, again, water percolating through soil or strata rich in microbes (such as surface waters), or water polluted with sewage, contains larger numbers of microbes than that derived from deep-seated springs, or from a non-polluted source.

In addition to the above mentioned conditions the number of microbes in any water depends upon the amount of organic matter present. A water rich in organic matter always contains a larger number of microbes (in a given volume) than a water almost free from such matter; but if the organic matter is rapidly converted by oxidation into the ultimate products of decomposition, the ordinary microbes of putrefaction are no longer able to obtain the necessary material for subsistence; nevertheless, the true water microbes, according to Meade Bolton (*Zeit. für Hygiene*, Bd. i., p. 76) and others, can still flourish and even multiply in distilled water. But, as Prof. P. F. Frankland (*Journ. Soc. Chem. Ind.*, 1887, vol. vi.) justly remarks, "it should be observed that when it is stated that an organism has multiplied in distilled water, it must be understood that this multiplication has doubtless taken place at the expense of those traces of organic matter which must of necessity be present in experiments of this kind."

As the bacteriological examination of water has now come to be a subject of great importance, I venture to describe a new bacteriological method for examining any sample of water; but before doing so it will be interesting to allude to the methods in use for the same purpose.

Methods for Examining Waters for Microbes.

The principal methods used for the qualitative examination of water for microbes are those of Prof. J. Burdon Sanderson (Reports of the Medical Officer of the Privy Council, 1870) and the late Dr. R. Angus Smith (*The Sanitary Record*, 1883, p. 344), while the methods used for the quantitative examination of water for microbes are (1) the plate-cultivation process, introduced by Dr. R. Koch (*Mittheilungen aus dem Kaiserlichen Gesundheitsamte*, Bd. i. in 1881, and (2) the process of fractional cultivation in bouillon or other liquid media, which is largely used by M. Miquel* and other French authorities.

1. *The Plate-Cultivation Method.*—This method consists in taking a known small quantity (say 1 c.c.) of the water and mixing it with melted nutrient gelatin (sterile)

contained in a stock-tube.* After shaking the mixture it is rapidly poured out upon a sterilised glass plate, then allowed to solidify, and finally placed in a damp chamber kept at about 22° C. After a few days' incubation, colonies make their appearance on and in the layer of gelatin. The gelatin plates are inspected every twenty-four hours, until the day when one or more of the colonies overlap one another, or until liquefaction of the gelatin destroys the solid *substratum*, and with it the collective seed-bed of microbes. The colonies so produced are counted by means of the eye or lens with the aid of Wolffhügel's apparatus.

2. *The Fractional-Cultivation Method.*—This method consists of two operations: (a) the dilution process, (b) the distribution of bouillon of the water diluted. To dilute the water the authorities of the Laboratoire de l'Observatoire de Montsouris (where this method is largely used), employ flasks varying in capacity from 30 to 2000 c.c. These flasks are covered with caps containing sterilised cotton-wool plugs. Each flask is half filled with a known volume of distilled water, which is then sterilised in a digester for more than an hour at 110° C. After agitation of the water under investigation, it is diluted with from 15 to 1000 c.c. of sterilised water (*i.e.*, according to its richness in microbes), and then 1 c.c. of the diluted sample is taken up by means of a sterilised capillary pipette. This quantity of water is distributed among 36 small flasks (each 15 c.c. capacity) containing sterilised beef bouillon. After the sterilised cotton-wool plugs have been replaced, all the flasks are placed in an incubator at 30–35° C. during a period of at least fifteen days, when the microbial colonies are counted.

It is stated that by this method there is no overlapping of the colonies, and a much higher temperature (during the incubation) can be used with liquid than with solid media. There is, however, a great drawback in using the fractional method, *viz.*, that the colonies undergo movements of translation; and consequently there are no means of preventing the overlapping which has been alluded to. Moreover, the ptomaines, &c., formed during the growth of some microbes† are dissolved, more or less, in liquid media, but not so when solid media are used, and in liquid media these products of microbial activity interfere with the growth of some microbes. This is a phenomenon which I have frequently observed.

Concerning the disadvantage of the low temperature at which Koch's nutrient gelatin melts (20° C.), it may be stated that Professor P. F. Frankland (*Journ. Soc. Chem. Ind.*, 1885, vol. iv.) has found that by using 150 grms. of gelatin instead of 100 grms.,‡ the melting-point of the nutrient gelatin is considerably raised. This was an important modification in the composition of Koch's solid medium, which I have taken advantage of in my own investigations.

There is no doubt, taking into consideration the *pros* and *cons*, that Koch's method is superior to that of fractional cultivation in bouillon. Even M. Miquel (*Annuaire de l'Observatoire de Montsouris*, 1889, p. 401), who uses the latter method, says: "Cette méthode (de M. Koch) est simple et très élégante; elle rend surtout de réels services quand il importe de séparer les microbes les uns d'avec les autres; elle permet le triage rapide des organismes contenus dans les eaux."

A New Method for the Examination of Water.

The following method, which I am desirous of bringing before the notice of chemists, bacteriologists, and others, is based on that of Dr. W. Hesse for the examination of

* If the original sample of water is very impure (*i.e.*, rich in microbes), it should be first diluted with sterilised distilled water.

† I have shown that some microbes of putrefaction are capable of giving rise to ptomaines in artificial media. (See *Comptes Rendus*, vol. cx., p. 416; *Bull. Soc. Chim. Paris*, Series 3, t. 7, p. 332; *Centralblatt für Bakteriologie*, Bd. vii., p. 808; and the references to my work in Gautier's "Cours de Chimie," t. 3, p. 268).

‡ The original quantity per litre, as used by Koch.

* "Annuaire de l'Observatoire de Montsouris," 1877-91; and his "Manuel Pratique d'Analyse Bactériologique des Eaux," 1891.

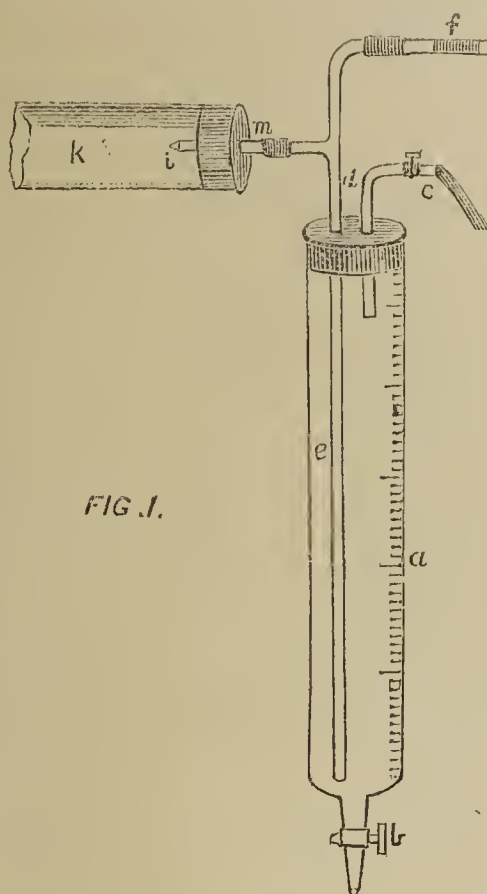


FIG. 1.

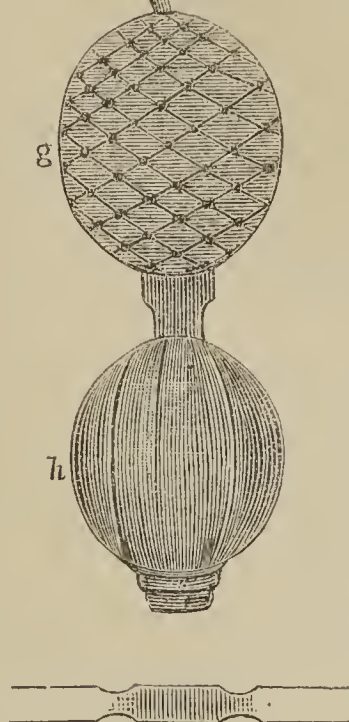


FIG. 2.



FIG. 3.

air (*Mittheilungen aus dem Kaiserlichen Gesundheitsamte*, Bd. 2).

The apparatus used in this new method is illustrated in Figs. 1 and 2. After having collected the sample of water with all the precautions mentioned by Frankland (*Journ. Soc. Chem. Ind.*, 1885, vol. iv.), 1 c.c. is introduced into the sterilised pipette *a* by suction at *c*; and, if necessary, this sample is diluted with a small quantity of sterilised distilled water by taking off the indiarubber tube *c*, and sending a stream of sterilised water through the tube *d* into the graduated pipette *a*. The taps *b* and *c* being closed, a current of sterilised air is passed to the bottom of the water by means of an ordinary hand spray-producer (*g, h*). This causes the sample of water to pass up the tube *e*, and finally to issue as a fine spray through the nozzle *i*. This spray is distributed over the surface of a glass tube (90 c.m. \times 5 c.m.) which has previously been coated internally with a thin layer of nutrient gelatin.

After the whole of the water has been sprayed into the tube, which is practically an easy operation, the small glass tube *m* is hermetically sealed, and the long cultivation-tube *k* is placed in an incubator, or a warm place for colonies to develop (Fig. 3 shows the colonies). The liquid particles introduced into the cultivation-tube *k* subside immediately, although they may be carried to three quarters of the length of the tube, the opposite end of which is plugged with sterilised cotton-wool.

The whole of the glass portion of the apparatus is readily sterilised by means of a hot-air steriliser, and previously washing in a solution of mercuric chloride (1 : 1000), alcohol, and sterilised water.* The indiarubber portion of the apparatus is sterilised by immersing it in a solution of mercuric chloride, and finally in sterilised water. It may be stated that the air from *g h* passes through a tight-fitting plug of sterilised cotton-wool, *f* (see also Fig. 2); in other words, it is filtered by this means, and the influx of air (through the apparatus) is also filtered through the cotton-wool plug at the opposite end of the cultivation-tube (not shown in the figures). In using this apparatus the strictest attention was paid to the sterilisation of it in every detail.

By this method I have obtained the following average results, which are compared with those obtained by using Koch's method. In each case the same sample of water was used. (See Table, next page).

The two series of experiments were conducted under similar conditions,—that is, as far as length of time of incubation, temperature, composition of the nutrient gelatin, &c. Concerning this method it may be remarked:—

(1) There is no burying, so to speak, of the microbes in the medium when the latter is melted, as is the case

* In the case of the cultivation-tube *k* before the introduction of the nutrient gelatin.

Samples of water collected from—	Colonies from 1 c.c. water by new method.	Colonies from 1 c.c. water by Koch's method.
River Thames at Richmond.. ..	6900	6200
Serpentine in Hyde Park, London	21300	21160
River Irwell, Manchester	8200	8100
River Medlock, Manchester	15320	15260
River Seine, Paris (taken near In- stitut de France)	18400	17980
River Seine, Paris (taken in vicinity of St. Cloud)	20300	20125
River Seine, Rouen.. .. .	27200	26700
Lake in the Parc des Buttes Chaumont, Paris	32100	31900
Lake in the Parc de Montsouris, Paris	34360	33920
River Witham, Lincoln.. .. .	11525	11050
Rain-water	644	620
Pond water (stagnant), Lincoln ..	40960	40240
River Lea, Birmingham	14980	14560

with Koch's method, the small particles of water being deposited on the solid medium. It appears that some aerobic microbes perish when immersed beneath the surface of the melted gelatin (Koch's method).

(2) The microbes deposited on the solid medium grow and multiply on the spot where they were first planted. There is not the smallest movement of translation; consequently this is a great advantage over the method of fractional cultivation in a liquid medium, and it is more accurate than Koch's method, in which the water is introduced by means of a pipette into the melted gelatin, whereby many microbes may become crowded together as the gelatin solidifies.

(3) The tube remains practically closed against any accidental contamination with microbes of the air. This is a great advantage over Koch's method, for in the latter method such contamination is possible during the preparation of the plate cultivation.

(4) The sample of water (of known volume) is introduced directly into the sterilised apparatus.

(5) By gently blowing air into the graduated tube (after spraying), every particle of moisture is sent into the tube *k*.

(6) The new method may appear to be favourable for the growth of aerobic microbes, and unfavourable for the growth of anaerobic microbes. But this is not so; for all the common forms peculiar to different kinds of water* readily make their appearance when this method is used.

In conclusion, it may be stated that this method has all the advantages of that of Koch, in addition to several others which have already been mentioned.

Explanation of the Plate.

FIG. 1 shows the general arrangement of the apparatus when ready for spraying the sample of water into the cultivation-tube. The indiarubber balloon (*h*) is compressed with the hand, and *g* is an air-receiver.

FIG. 2 is an enlargement of *f* in Fig. 1, and shows the way of fixing the cotton-wool plug for filtering the air.

FIG. 3 shows one end of the cultivation-tube with colonies after several days' incubation.

The Chicago Exhibition.—We are requested to state that the New York Section of the American Chemical Society has appointed a Committee, of which Dr. H. Carrington Bolton is Chairman, to receive distinguished chemists who may pass through New York on their way to or from Chicago. Chemists arriving in New York are requested to send their names and addresses to Professor Morris Loeb, University of the City of New York, who is Secretary of the Committee.

* See the author's "Manual of Bacteriology," p. 287 (W. Heinemann).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 20th, 1893.

Dr. ARMSTRONG, President, in the Chair.

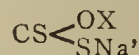
(Concluded from p. 226).

*2. "The Interaction of Alkali Cellulose and Carbon Disulphide: Cellulose Thiocarbonates." By C. F. CROSS, E. J. BEVAN, and C. BEADLE.

Alkali cellulose has been further investigated by the authors, both in the form known as "mercerised" cellulose (cotton) and in the form of gelatinous hydrates which dissolve in alkaline solutions. The corresponding benzoates which have been prepared afford evidence as to the number of active OH groups; the maximum appears to be four, cellulose being expressed as $C_{12}H_{20}O_{10}$.

Cellulose thiocarbonates result from the interaction of alkali cellulose and carbon disulphide in the molecular proportions $C_{12}H_{20}O_{10} : 4NaOH : 2CS_2 : 30-40H_2O$. The product swells up enormously on treatment with water, and finally completely dissolves, but undergoes change, hydrated cellulose and products of interaction of the alkaline hydrate and carbon disulphide being formed.

From the study of the composition of a large number of these products, the authors are led to assign to the series of compounds the general formula—



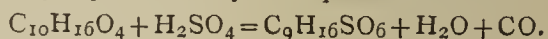
X representing the cellulose "residue" or rather an alkali cellulose residue or radicle of variable dimensions.

These thiocarbonates of cellulose yield solutions of extraordinary viscosity, and from the property they possess of undergoing change, regenerating cellulose, promise extended applications. The further investigation of the compounds is in progress.

In conclusion, the bearings of the results and other recent contributions to cellulose chemistry are discussed with reference to the molecular constitution of the typical members of the series.

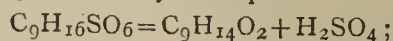
3. "Sulphocamphylic Acid." By W. H. PERKIN, jun.

In the course of a series of researches on camphoric acid and its derivatives, the author has for some time been engaged in submitting to detailed examination the sulphocamphylic acid which Walter (*Fahresb.*, xxi., 272; xxiv., 392) first prepared by heating camphoric acid with sulphuric acid. In the formation of this acid, quantities of carbonic oxide are evolved, the decomposition being apparently represented by the equation—



After carefully verifying the formula of sulphocamphylic acid by the analysis of the acid and of some of its salts, the author next studied the behaviour of the acid on distillation. When small quantities of the acid are rapidly heated in small retorts, vigorous decomposition takes place, a small quantity of a colourless oily substance, which soon solidifies, passing over, a large amount of carbonaceous matter being left in the retort.

After re-crystallisation from formic acid, the solid product melts at $134-135^\circ$; on analysis it gives numbers agreeing with the formula $C_9H_{14}O_2$, and is a monobasic acid, its formation from sulphocamphylic acid being apparently represented by the equation—



it yields a silver salt of the formula $C_9H_{13}AgO_2$. The acid distils with only slight decomposition, and volatilises with steam; it dissolves in cold sulphuric acid without decomposing, but on warming the solution at 90° a sulphonic acid is readily formed: this appears to be re-

generated sulphocamphylic acid, but no analysis of the product has as yet been carried out.

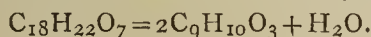
A neutral solution of the sodium salt of sulphocamphylic acid is readily oxidised by potassium permanganate at 0°, forming a variety of products: from these the author has succeeded in isolating small quantities of a beautifully crystalline compound, melting at 254°, which on analysis was found to possess the remarkable formula $C_{18}H_{22}O_7$. This substance is a dibasic acid, the silver salt having the formula $C_{18}H_{20}O_7Ag_2$; when heated at 140° the acid loses 1 mol. prop. of water, and is converted into a compound of the formula $C_{18}H_{20}O_6$.

The *dimethylic salt*, prepared by treating the compound of the formula $C_{18}H_{22}O_7$ with methyl alcohol and sulphuric acid has the formula $C_{20}H_{24}O_6$, instead of $C_{20}H_{26}O_7$ as might have been expected.

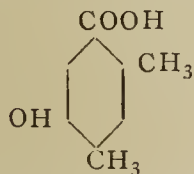
The compound of the formula $C_{18}H_{22}O_7$ affords a *dihydroxime*, $C_{18}H_{22}N_2O_6$, which crystallises from ether in scales which do not melt at 250°. Excess of acetic anhydride converts this hydroxime into a *monoacetate*, $C_{18}H_{21}N_2O_6(C_2H_3O_2)$, m. p. 195°. By the action of phenylhydrazine it is converted into a dihydrazone, $C_{30}H_{34}N_4O_5$; this compound crystallises from acetic acid in brilliant red prisms which decompose at 232°.

The acid of the formula $C_{18}H_{22}O_7$ is readily reduced by sodium amalgam, combining with 2 atoms of hydrogen and losing 1 mol. of water, the product having the composition $C_{18}H_{24}O_6$. This reduction product is a dibasic acid, which does not melt at 300°; the *silver salt*, $C_{18}H_{22}Ag_2O_6$, was analysed.

Among the many remarkable decompositions of the substance of the formula $C_{18}H_{22}O_7$, the investigation of which is not concluded, the behaviour of this acid towards sulphuric acid is perhaps the most interesting. The acid readily dissolves in concentrated sulphuric acid; if the solution be warmed at 90–95° decomposition rapidly takes place, and on pouring the product into water a yellow flocculent substance separates, which is a new monobasic acid of the formula $C_9H_{10}O_3$; the formation of this acid may be represented by the equation—

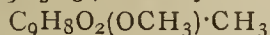


A careful investigation of this compound has proved that it is a *hydroxymetaxylencarboxylic acid* of the constitution represented by the formula—



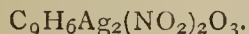
In the course of the prolonged investigation of this acid which was necessary before its constitution could be determined, the following derivatives were prepared and analysed:—

Silver salt, $C_9H_9O_3Ag$; *dimethylic salt*,—



(oil); *methylic salt*, $C_9H_8O_2(OH) \cdot CH_3$ (m. p. 149°); *iso-methylic salt*, $C_9H_8O_2(OCH_3)H$ (m. p. 171°); *diethylic salt*, $C_9H_8O_2(OC_2H_5) \cdot C_2H_5$ (m. p. 51°); *ethylic salt*, $C_9H_8O_2(OH) \cdot C_2H_5$ (m. p. 135°); *isoethylic salt*, $C_9H_8O_2(OC_2H_5)H$ (m. p. 174°).

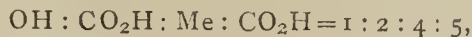
A *dinitro-acid* of the formula $C_9H_8(NO_2)_2O_3$, formed by the action of nitric acid; this crystallises in yellow needles which melt at 203–205°; it behaves as a dibasic acid, giving a silver salt of the formula—



When exposed to the action of bromine vapour, it is converted into a *dibromo-derivative*, $C_9H_8Br_2O_3$, which crystallises in colourless prisms and melts at 205°.

The isomethylic salt is readily oxidised by an alkaline solution of potassium permanganate, yielding a substance of the formula $C_7H_5(OCH_3)(COOH)_2$, which crystallises in colourless needles melting at 250°. When heated with

a fuming solution of hydrogen iodide, this dibasic acid is readily decomposed, yielding the corresponding phenolic compound, $C_7H_5(OH)(COOH)_2$, which on investigation has proved to be identical with the *hydroxymethylterephthalic acid* of the formula—



prepared by Jacobsen (*Ber.*, xvi., 191). This result proves that the acid of the formula $C_9H_{10}O_3$ has the constitution assigned to it above, i.e., that of hydroxymetaxylene-carboxylic acid ($COOH : CH_3 : CH_3 : OH = 1 : 2 : 4 : 5$).

The author hopes in a short time to be able to publish the details of these and many other experiments not mentioned in this abstract, and to be in a position to explain the relationship between the compounds represented by the formulæ $C_{18}H_{22}O_7$ and $C_9H_{10}O_3$; as also to suggest a constitutional formula for sulphocamphylic acid.

4. "Magnesium Diphenyl." By LOTHAR MEYER.

W. R. Hodgkinson, in a recent note (*Proc. Chem. Soc.*, 1893, p. 80), refers to a substance not yet obtained pure which he suggests may be magnesium phenyl; this induces me to state that magnesium diphenyl was prepared in my laboratory last year by Hermann Fleck, and described by him in his inaugural dissertation ("Ueber Magnesium Alkyle"; Tübingen, 1892), and that an account of his work will be published in Liebig's *Annalen*.

Magnesium diphenyl, $MgEt_2$, is obtained by the interaction of magnesium and mercury diphenyl at 200–210° in the form of a very voluminous powder, insoluble in all ordinary liquids, but soluble in a mixture of ether and benzene. It is spontaneously inflammable; on slow oxidation it yields a phenate; water converts it into benzene and magnesium hydrate; it affords bromobenzene and magnesium bromide on treatment with bromine, triphenylmethane on treatment with benzal chloride, and diphenylphosphine chloride and more complex compounds when subjected to the action of phosphorous chloride. It has the advantage over mercury diphenyl that it readily exchanges both phenyls for other radicles, and does not yield a compound corresponding to mercury phenyl chloride. The study of the magnesium alkyls is being continued in the Tübingen Laboratory.

5. "The Formation of Pyridine Derivatives from Unsaturated Acids." By S. RUHEMANN, Ph.D.

An account is given of the continuation of previous work by the author on the same subject. It is now shown that *ethylic methylglutamate* is converted by aqueous ammonia into *methylmalonamide* and *ethylic amidoethylenedicarboxylate*, and that phenylhydrazine acts on it, forming *ethylic methylmalonate* and the ammonium compound of the *pyrazolon*,—



which has been previously described.

Ethylic methylglutamate is converted by the action of aqueous ammonia into β -methyl- $\alpha\alpha'$ -dihydroxypyridine; on reduction with zinc dust, the compound furnishes β -picoline; on oxidation with ferric chloride, it affords a yellow colouring matter.

Ethylic ethylglutamate is converted by aqueous ammonia into *ethylmalonamide* and *ethylic amidoethylenedicarboxylate*; and by phenylhydrazine into a *pyrazolon* and *ethylic ethylmalonate*.

When heated with aqueous ammonia in a closed tube at 100°, *ethylic ethylglutamate* is converted into *ethylic dihydroxypyridine*, which yields a yellow colouring matter, probably a hydroxyquinone, on oxidation with ferric chloride.

6. "Chlorinated Phenylhydrazines." Part II. By J. T. HEWITT, Ph.D.

The author, in continuation of his previous work, describes the *sulphate* and *oxalate* of *ortho*chlorophenyl-

hydrazine. Unlike the meta- and para-derivatives, this hydrazine does not form a urazole when heated with biuret. The ethylic salt of the hydrazone of pyruvic acid occurs in yellow needles melting at 68°, not at 168° as previously stated; it is insoluble in alkalis.

Metachlorophenylhydrazine, which has been prepared and described by Willgerodt and Mühe, forms a crystalline hydrochloride, sulphate, and nitrate. A solution of the hydrochloride and potassium cyanate interact to form a semicarbazide melting at 155°; the corresponding thio-semicarbazide is obtained when phenyl mustard oil is used. The hydrazine furnishes a urazole when heated with biuret.

The metachlorophenylhydrazone of benzaldehyd crystallises in colourless needles melting at 133–134°; the corresponding hydrazone of pyruvic acid is crystalline, and melts at 163°.

Parachlorophenylhydrazine is also shown to form a similar semicarbazide and hydrazones of benzaldehyd and pyruvic acid.

7. "The Oxidation of Tartaric Acid in Presence of Iron." By H. J. H. FENTON, M.A.

If a small quantity of hydrogen peroxide be added to a solution of tartaric acid containing a trace of ferrous salt, a yellow colour is produced which changes to violet on adding alkali; an excess of the peroxide must be avoided. As other organic acids do not behave in this manner, the interaction may be utilised in detecting tartaric acid. The violet colour is discharged by acids, sulphuric acid producing a transient green colouration, and is reproduced by alkali.

The compound which gives the colour with ferric salts is crystalline, and appears to be represented by the formula $C_2H_2O_3$. It is best obtained by dissolving tartaric acid in a limited quantity of boiling water, and then adding about $\frac{1}{10}$ th of its weight of reduced iron; the liquid is then heated until clear. After the solution has been well cooled, hydrogen peroxide is carefully added drop by drop, the temperature being maintained constant until the liquid is nearly black; slightly hydrated phosphoric oxide is next added in small quantities at a time, the mixture being still well cooled, and finally the compound is extracted with ether. The ether is then distilled off, and the residue mixed with cold water; the resulting white powder is washed with a small quantity of cold water. The compound is a powerful reducing agent, and behaves as a ketone with phenylhydrazine, hydroxylamine, and hydrogen cyanide. The author is further investigating the properties and constitution of the product in question.

8. "The Inertness of Quicklime." By V. H. VELEY.

The conditions under which calcium carbonate is formed from lime and carbon dioxide have been investigated by Debay, Raoult, and Birnbaum, with Mahn: but the experiments of these authors are neither described in detail, nor were they made under comparable conditions.

The experiments recorded in the paper were conducted on a much larger scale than heretofore, and the amount of combination between the lime and carbon dioxide as dependent on the conditions (1) of moisture, (2) of temperature, is investigated. It is shown that the combination is incomplete, not only with lime to which 11 per cent of water is added, but even with the hydrate; the presence of 10 per cent free water in the hydrate increases the absorptive power nearly fourfold. Dry carbon dioxide combines with lime to a slight extent at 300°, to a greater degree at 350°, and fairly completely at 420° (melting point of zinc; cf. Birnbaum and Mahn).

The conditions of the formation of calcium sulphite from lime and sulphur dioxide have been studied by Birnbaum and Wittich, who do not, however, give any quantitative results.

It is here shown that lime and sulphur dioxide, when dry, begin to combine at about 300°, and more completely at 352°; but at a higher temperature the resulting sulphite

is decomposed into sulphate and sulphide, and by the interaction of the latter and the sulphur dioxide sulphur is formed.

There is a great similarity in the behaviour of dry carbon and sulphur dioxide as regards the amounts of them absorbed by lime under the same conditions of temperature. Incidentally it is noted that quicklime does not absorb nitrous fumes at ordinary temperatures.

It is proposed to continue these investigations.

9. "The Products of the Interaction of Tin and Nitric Acid." By C. H. H. WALKER.

This investigation is a continuation of the investigations of Veley on the conditions of the interactions of metals and nitric acid.

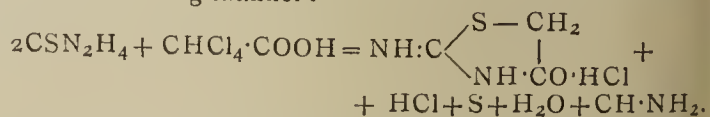
Since the work was commenced, a paper by Clemente Montemartini on the same subject has appeared.

It is generally stated in manuals on chemistry that metallic tin dissolves in nitric acid, forming both a stannous and stannic salt, according to the conditions of temperature and concentration of acid, but it does not appear that this statement is based on quantitative investigations.

In the paper determinations are given of the amounts of stannous salt formed according to the conditions of (1) mass of metallic tin; (2) temperature; (3) concentration of acid. It is shown that the proportion of stannous salt formed is but little affected by the mass of tin, and in the case of dilute acids by increase of temperature, but with more concentrated acids the effect is more marked, so that an alteration of a few degrees reduces the amount of stannous salt to *nil*. Increase of concentration of acid, other conditions remaining the same, decreases the proportion of stannous salt. The white, or yellowish white, substance deposited from fairly concentrated solutions is a hydrated stannic nitrate of rather indefinite composition (cf. Clemente Montemartini). The average value of a number of analyses corresponding most nearly with a formula $Sn(NO_3)(OH)_3$. The substance appears to slowly decompose on exposure, so that the composition varies not only with the time elapsing between its production and analysis, but also according to the method of purification adopted to eliminate nitric acid.

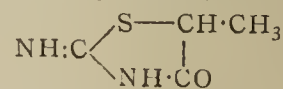
10. "Interaction of Thiourea and some Haloid Derivatives of Fatty Acids." By AUGUSTUS E. DIXON, M.D.

On warming thiourea with dichloroacetic acid, either alone or in solution (in water or in dilute spirit), hydrogen chloride is evolved, sulphur and thiohydantoinic acid are deposited and the filtered solution on standing yields orthorhombic crystals of thiohydantoin hydrochloride. The formation of this latter substance may be expressed in the following manner:—



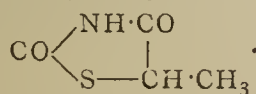
In the case of trichloroacetic acid, complete decomposition occurs, carbonic anhydride, hydrogen chloride, hydrogen sulphide, sulphur, and chloroform being produced. Ethylic trichloroacetate in boiling alcoholic solution has scarcely any action.

α -Monochlor- (or brom-) propionic acid and thiourea readily interact, yielding the hydrochloride (or hydrobromide) of methylthiohydantoin,



The latter compound, separated from its salts by caustic alkali, crystallises from alcohol in brilliant, vitreous prisms; it melts at 205°–206° (uncorr.), but is decomposed. It is not desulphurised, either by treatment with silver salts or with alkaline lead solution; on boiling with baryta-water it yields methylthioglycollic acid. On boiling with chlorhydric acid, ammonium chloride is produced, together with a substance crystallising in

needles; this was not obtained in a pure condition, but from the mode of production, and the ready manner in which it undergoes conversion into methylthioglycollic acid, it must be β -methylthioxythiazole,



NOTICES OF BOOKS.

A Manual of Dyeing. For the Use of Practical Dyers, Manufacturers, Students, and all interested in the Art of Dyeing. By EDMUND KNECHT, Ph.D., F.I.C.; CHRISTOPHER RAWSON, F.I.C., F.C.S.; and RICHARD LOEWENTHAL, Ph.D. Vol. II. (Second Notice). London: Charles Griffin and Co., Limited.

IN this volume the authors consider the artificial organic colouring matters, arranged in the following groups:—Direct cotton colours, basic colours, acid colours, eosins and rhodamines, mordant colours, and miscellaneous group, comprising aniline-black and, among others, indigo.

In the first group figures *Erika*, which, we submit, might more fittingly be written *Erica*. The direct cotton colours are in many cases inapplicable on account of their liability to bleed.

The basic colours are so named because their chromophorous group is contained in the bases. Their tinctorial power is in many cases exceptionally high. It is satisfactory that the authors are able to affirm that in the manufacture of magenta the arsenical process has been to great extent relinquished in favour of nitrobenzene process.

The acid colours are sub-divided into three groups: the nitro-compounds, the azo-compounds, and the sulphonated basic colours. The eosins and rhodamines are distinguished for remarkable brilliance, and are, in solution, more or less fluorescent. In some cases their fluorescent character is an objection, and they are for many purposes too fugitive and too expensive.

The mordant colours dye fibres only with the aid of metallic mordants. Their type is alizarin, and the important process of Turkey-red dyeing turns on its use.

In the history of aniline-black the part taken by Light-foot scarcely comes into sufficient prominence.

As regards the manufacture of artificial indigo it is admitted that Bayer's expectations have not been realised, and that there is little demand for propiolic acid. Whether Heymann's method of manufacturing artificial extract of indigo—which the authors call indigo carmine—will prove successful the future must show.

The machinery used in dyeing forms the subject of an elaborately illustrated section.

Of no less importance is a part devoted to experimental dyeing, which is especially necessary in case of novel colours.

Concerning the recognition of the fastness of colours to light, we find some very appropriate remarks on the discrepancy of results obtained by different experimentalists, and some suggestions are thrown out relating to a uniform procedure.

The analysis and valuation of dye wares are very fully and ably treated. For most wares comparative dye tests are still almost the only method available. It is admitted, however, that the colorimeter will often be found very useful in the examination of dyes as a check upon the dye tests. For indigo, chemical analysis is pronounced necessary.

"The experimental error involved in making dye tests is great in comparison with that of an ordinary chemical analysis. Let the conditions be ever so favourable, the eye is incapable of discriminating between two shades of

the same colour if the difference is less than a certain small amount which in a chemical analysis would be considered great." It was hoped that the spectroscope would have supplied us with a physico-chemical means of deciding on the value of colours, but so far this expectation has not been fulfilled.

Vol. III. contains the colour patterns in illustration of the text. They may fairly be pronounced excellent. The work of Messrs. Knecht, Rawson, and Loewenthal will prove a boon to all persons concerned with the tinctorial industries, and we feel sure that it will be widely appreciated.

CORRESPONDENCE.

PURIFICATION OF WATER USED FOR STEAM-BOILERS.

To the Editor of the Chemical News.

SIR,—I shall consider it a great favour if you will insert in your next issue the following reply to some observations made on our Water Purification Process by R. Jones, Ph.D., in the CHEMICAL NEWS, vol. lxxvii., pp. 171 and 185.

I note that the absolute reliability and automatic action of our process, which is used to satisfaction all over the Continent in over four hundred works is not contested. Dr. Jones contends, however, that the possibility of a slight excess of free alkali increased by concentration may be very detrimental to the boiler, and in support of this assertion he enumerates several instances in which boilers are said to have been attacked by the presence of free alkali in the feed-water. We must strongly protest against this possibility for the following reasons:—

A very bad water may require as much as 300 grms. of caustic soda per cubic metre, and if we suppose that on account of variations in the composition of the impure water as much as 10 per cent of the alkali should go undecomposed into the feed-water, it would represent an addition of 0.00003 per cent; and if we take it that this amount of free alkali is increased by concentration tenfold, we should still arrive at a homœopathic dilution. It is easy and inexpensive enough to blow off the boiler occasionally in order to avoid even this possible concentration.

For this reason we need not enlarge upon the question which still seems open to slight doubt: Whether or not iron plates are very slightly attacked in the long run by a concentrated boiling solution of alkali? We are fully acquainted with the observations which have led some people to the wrong conclusion of some boilers being attacked. The boiler plates, when the boiler has been fed for some time with very bad water, and covered with incrustation, are subject to considerable overheating, which causes rivets and bolts to loosen. The tightening of the joints is, however, very effectually done by the incrustation, so that these defective places remain unobserved by the stoker.

If such a boiler is properly knocked out and cleaned before the application of our system, and the small amount of incrustation in the joints gets gradually dissolved, the boiler is bound to leak. After all, this proves nothing but that before the wholesome application of a reliable water purification plant, the boiler should be closely inspected and repaired.—I am, &c.,

C. HARZER,

Representative of A. L. G. Dehne,
Halle on Saale.

Billiter Bldgs., Billiter St.,
London, E.C.

DANGEROUS TRADES.

To the Editor of the Chemical News.

SIR,—An article on this subject in the CHEMICAL NEWS, vol. lxvii., pp. 179 and 203, leads me to enclose you some paragraphs from a paper I have lately published on the subject of the methods used in Germany for the protection of the workpeople. I should be glad if you could find space for them.—I am, &c.,

M. CAREY LEA.

The first step taken in Germany was to appoint Commissions which investigated all the dangerous trades and reported very fully on the evils found and their remedies. The entire empire was then divided into fifty-one districts, for each of which a competent inspector was appointed. These inspectors have a right to examine every part of all the factories and workshops, and to require the establishment of all such reforms as they judge necessary. They confer not only with the employer, but with the workmen. A few instances will serve to show the beneficial effects which have resulted from this system.

In the district of Alsace-Lorraine 663 factories were inspected, out of which 286 were reported as having insufficient ventilation. Out of these 286 factories 209 were for textile industries. Much improvement was being made by the adoption of the system of ventilating with warm and moist air. The introduction of electric lighting has done much to improve the atmosphere of the work-rooms.

In the manufacture of mirrors great improvement in the health of the workpeople has been brought about by the use of silver instead of mercury for coating glass. In the town of Furth the mirror factory is reported as using silver exclusively for the mirrors sent to North America, and for about two-thirds of its entire product. At this factory the number of days of illness caused by mercurial poisoning in 1885 was 4074; in 1889 it was 1003. In 1890 this was reduced to 148, and since May, 1890, there have been no cases at all. When the serious nature of mercurial poisoning is considered, the great improvements brought about partly by the use of a less poisonous metal and partly by better methods, can be understood.

In the district of Cassel-Baden the manufacture of chrome gave rise to sickness among the workpeople. By improved methods the number of sick days was reduced in one year from 2865 to 899, so that at present the time lost by sickness by those actually engaged in the factory barely exceeds the proportion of loss among the outdoor workmen, masons, carpenters, laborers, &c.

In the great lead works at Tarnowitz, in the district of Oppeln, efforts have been made to check the malignant lead poisoning caused by the escape of lead fumes. This has been done by connecting all the different furnaces with a powerful ventilator, which draws out the fumes by exhaustion and forces them into a tall chimney. Arrangements are also made for purifying the gases from the lead which they contain. The effect of these changes on the health of the workpeople has been very remarkable. The number of sick days has been reduced to one-sixth of what it was formerly.

In the manufacture of phosphorus matches, the cases of constitutional injury by phosphorus poisoning have been very greatly reduced in number.

The manufacture of mineral fertilisers is attended with danger in all cases where the phosphate rock contains fluor-spar. Such rock when treated with sulphuric acid disengages vapours of hydrofluoric acid which are very injurious to the lungs and also destructive to vegetation. At a factory in the district of Breslau-Liegnitz this danger is completely overcome, and even a profit is made, by bringing the hydrofluoric vapours into combination, and thus obtaining artificial cryolite.

The fouling of streams by the drainage of factories is in all manufacturing districts a source of much trouble.

The chemicals used are for the most part injurious to the water in every way, rendering it unfit for drinking, and tending to destroy all animal life contained in it. As a single example it may be mentioned that it has been ascertained by actual trial that one part of burnt lime introduced into 100,000 parts of water in a river is sufficient to kill all the fish contained in it.

Stringent measures have been taken in Germany to diminish this evil, though in some cases, and particularly in the manufacture of beet-sugar, it has proved very difficult to find effectual means. But by the use of chemicals it can be accomplished. The Strobnitz factory, which works up 70,000 tons of beets each season, and whose waste-water amounts to over 1000 gallons per minute, purifies this so thoroughly that a specimen taken by the inspector remained three weeks in a warm room odourless. In some cases it has proved that waste-waters containing organic matter which were very injurious to streams by reason of the fermentation which they set up, were found, on the other hand, very useful to fertilisation by means of irrigation. For example, a starch factory on the River Werra caused much damage by fouling the water with the waste products of the manufacture. But when these products were carried to the neighbouring farms their fertilising qualities proved so valuable that the demand for them could hardly be met.

These facts, all derived from official sources (the reports of the inspectors epitomised in the *Chem. Zeitung*), serve to show what valuable reforms can be effected through the agency of intelligent inspection.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 18, May 1, 1893.

Determination of the Specific Heat of Boron.—Henri Moissan and Henri Gautier.—The mean specific heat of boron between 0° and 100° is found experimentally as 0.3066. This figure is higher than that of Weber. The difference goes on in the same direction up to the temperature of 234°. The value 0.3066 thus obtained, if multiplied by the atomic weight of boron, 11, gives the result 3.3 in place of 6.4, the figure admitted by the law of Dulong and Petit. This atomic heat increases with the temperature, and if we extrapolate the above results up to a temperature of 400°, we find for the atomic heat a figure close upon 6.4.

Rock Phosphates of Animal Origin, and on a New Type of Phosphorites.—Armand Gautier.—The author has analysed the deposits found in the Department Herault, and finds them similar to phosphorites, hitherto found only in certain islands of the Caribbean Sea.

Sanitary System adopted by the Hygienic Conference at Dresden.—M. Brouardel.—The delegates propose to lay an embargo upon rags, old clothes, and dirty linen coming from suspected territories. Portugal, Greece, and Turkey, however, adhere to the old system of quarantine.

Researches to Determine Bases for a New Method of Detecting the Sophistication of Butters by Margarine, whether used alone or in a Mixture with other Fats, Animal or Vegetable.—A. Houzeau.—The substance of this bulky paper will be inserted as early as possible.

Densities and the Molecular Volumes of Chlorine and Hydrochloric Acid.—A. Leduc.—It appears to the author that if we compare the molecular volumes of any

two gases under normal conditions, the one which is nearest to its critical point must have the smaller volume.

Decrease of the Coefficient of Expansion of Glass.—L. C. Baudin.—If we consider a thermometer uniformly heated in all its parts, the capacity of the stem diminishes uniformly in the same proportion as the volume of the bulb. To the decrease of the capacity of the thermometric channel there corresponds a proportional contraction in the length of the stem. If, with M. Benoit, we accept 0.000021552 as the coefficient of the cubic expansion of green glass, it becomes about 0.00002096 after re-heating, having raised the zero by 26.2°.

Decomposition of Oxalic Acid by Ferric Salts under the Influence of Heat.—Georges Lemoine.—The phenomena depend on the decomposition of ferric salts by water as established by Debray and Berthelot. A solution of ferric oxalate, if heated to 100°, is slightly decomposed. Fe_2O_3 , momentarily soluble, is set at liberty, reduced by oxalic acid, and yields CO_2 . If there is an excess of oxalic acid, it interferes with the decomposition of the ferric salt, and consequently the final reaction, producing CO_2 . The extensive alteration of ferric chloride by water is the turning-point of all these reactions.

Contribution to the Study of the Leclanche Battery.—A. Ditte.—This memoir is not suitable for useful abstraction.

Alkaline-Earthy Fluorides.—C. Poulenc.—The author has examined the strontium, barium, and calcium fluorides. He has studied the action of gaseous hydrofluoric acid upon strontium chloride, the action of alkaline chlorides upon amorphous strontium fluoride, that of the hydrofluoride of potassium fluoride upon amorphous strontium fluoride, and that of strontium chloride upon potassium fluoride hydrofluoride. Crystalline strontium fluoride forms regular octahedral crystals.

Determination of Phosphoric Acid.—A. Villiers and Fr. Borg.—This paper will be inserted in full.

On Licarene, derived from Licareol.—Ph. Barbier.—Licareol is transformed by loss of water into the cyclical hydrocarbonated group, $\text{C}_{10}\text{H}_{16}$, when the dehydration is effected by means of acetic anhydride, and into $\text{C}_{10}\text{H}_{18}\text{Cl}_2$, if it takes place under the influence of dry, gaseous hydrochloric acid. The carbide, $\text{C}_{10}\text{H}_{16}$, is an active limonene, whilst the compound $\text{C}_{10}\text{H}_{18}\text{Cl}_2$ is its inactive hydrochlorate.

On a Vegetable Nucleine.—P. Petit.—The nucleine which the author has extracted from barley differs from the animal nucleines of Kossel, Liebermann, and Bunge, by containing no sulphur. In solutions of common salt it swells up and becomes greyish. It does not give Millon's reaction, and is soluble in alkalis. If heated under pressure with water (four atmospheres) it dissolves to a pale yellow liquid, which is a very favourable medium for microbia. The author suspects the presence of a compound analogous to this nucleine in the black matter of the soil.

Periodicity of the Odoriferous Property in the Fatty Series.—Jacques Passy.—The variations of the odoriferous power point to a more complex law than the author had at first suspected. With the fourteenth term of the series of fatty acids the odour reaches the limits of perceptibility for us.

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Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 6.

Preparation of Absolutely Pure Hydrogen Peroxide.—Léon Crismer.—(From the *Bull. Soc. Chim.*.)

Preservation of Normal and Decinormal Oxalic Acid.—R. W. Gerland.—(From the *Journ. Soc. Chem. Industry*.)

The Colouration which Sodium Hypobromite Assumes if kept in some Glass Bottles.—G. Denigès (*Journ. Pharm. Chimie* and *Chemiker Zeitung*).—The author found that such a solution quickly lost its golden yellow colour in a reddish brown glass. He observed that this change of colour is due to the presence in the glass of manganese, which is converted into an alkaline permanganate. The hypobromite is still fit for analytical uses.

On Rare Earths.—Lecoq de Boisbaudran (*Bull. Soc. Chim. de Paris*).—Already inserted.

Determination of Iron in Ferric Salts.—Alonzo C. Campbell.—(From the *Journal of Analytical Chemistry*.)

Volumetric Determination of Mercury.—Rodolphe Namias (*Gazz. Chimica* and *Chem. Zeit.*).—The mercury must be present as chloride or be transformed into this state. The solution of mercuric chloride is mixed with a solution of stannous chloride until all the mercury is thrown down as mercurous chloride. As indicator the author uses a freshly-prepared solution of sodium molybdate, with which filter-paper is moistened. The latter turns blue on spotting with the solution of mercury in question as soon as a slight excess of stannous chloride is present. The solution of stannous chloride is prepared by dissolving from 2 to 3 grms. of pure tin in hydrochloric acid and diluting to 1 litre. The standard is ascertained with solution of iodine, or, preferably, with from 0.2—0.4 grm. pure mercuric chloride, which is dissolved in 50 c.c. water and 0.5 c.c. hydrochloric acid.

Separation of Mercury from the Metals of the So-called Arsenic and Copper Group.—K. Bülow.—(An Inaugural Dissertation).—Already inserted.

Determination of Phosphoric Acid by the Molybdenum Method.—O. Foerster (*Chem. Zeit.*).—In the method in question, the complete washing of the ammonium-magnesium phosphate is very difficult, as both the precipitate and the filter retain traces of ammonium molybdate with great obstinacy. Further, the impurity which almost always appears as a slight turbidity of the liquid on dissolving the ammonium phosphomolybdate in ammonia passes into the precipitate on throwing down the magnesium ammonium phosphate in the cold. These defects, according to Foerster, may be almost entirely avoided if the ammoniacal solution of the ammonium phosphomolybdate is gently heated before adding the magnesia mixture. The precipitate is then crystalline, much less bulky, and can be easily thrown upon the filter, so that it is much more easily washed. The impurity which occasions a turbidity on dissolving the ammonium phosphomolybdate in ammonia does not pass into the precipitate, and on washing runs through the filter. In order to throw down small quantities of ammonium-magnesium phosphate, which may remain in solution on precipitation in heat, the liquid when cold is once more thoroughly stirred up before filtration. For washing the precipitate it is convenient to use a solution of ammonium nitrate (50 grms. in 1 litre of liquid ammonia at 2.5 per cent). The residue on ignition is then almost white.

Volumetric Determination of Bromine along with Chlorine and Iodine.—Norman McCulloch.—(From the *CHEMICAL NEWS*.)

Determination of Sulphur in Iron and in the Sulphides Decomposable by Hydrochloric and Sulphuric Acids.—L. L. de Koninck and Ed. Dietz.—(From the *Revue Universelle des Mines Metallurgie*).—Already inserted.

Determination of Sugar.—A series of extracts from the *Zeit. Angew. Chemie*, the *Chemiker Zeitung*, the *Journ. Anal. Chemie*, the *Bull. Soc. Chim. de Paris*, and other journals.

Determination of Glycerin in Wine.—B. Proskauer.—This paper will be inserted in full.

Occurrence of Boric Acid in Caustic Alkalies.—F. P. Venable and J. S. Callison.—(From the *Journ. Anal. Chem.*).

Preparation of a very Efficient Platinum Black.—O. Loew (*Berichte Deutsch. Chem. Gesellschaft*).—The author dissolves 50 grms. platinum chloride in water so as to make up from 50 to 60 c.c., and mixes it with 70 c.c. of a 40 to 45 per cent formaldehyd. In the mixture he dissolves 50 grms. caustic soda and adds an equal weight of water. The greater part of the metal is at once deposited. After twelve hours the mixture is filtered through a suction-filter, when a yellowish liquid passes through the filter and on boiling deposits a little platinum. A part of the precipitate dissolves on washing as soon as the salts are chiefly removed, forming a deep black solution. The washing is therefore interrupted until the incipient process of oxidation is completed. Oxygen is freely absorbed, and the temperature rises from 36° to 40°, whilst a crackling sound is heard and small gas-bubbles escape. The platinum black, thus rendered loose and porous, is completely washed, pressed, and dried over sulphuric acid.

Action of Sublimate upon Zinc.—H. Börntäger (*Pharm. Central Halle*).—A development of hydrogen much accelerated by means of platinum chloride is at once arrested if one or two drops of a 10 per cent solution of mercuric chloride is added to the sulphuric acid in contact with the zinc. The mercury nitrates do not interfere with the development of hydrogen.

Sensitive Turmeric Paper.—According to the *Bolletino Farmaceutico* a very sensitive paper is obtained by dipping slips of neutral filter paper in a solution of tincture of turmeric (1:7). When quite dry they are steeped in 2 per cent potassa-lye and quickly washed with pure distilled water. The papers when dry are packed up in tin-foil. This paper reacts with 1 part of hydrochloric acid in 150,000 parts water.

Preparation of a very Sensitive Indicator from Litmus.—J. Lüttke (*Apoth. Zeitung*).—The author extracts 100 grms. commercial litmus three or four times successively with warm water, and evaporates the united extracts down to 200 c.c. The concentrated solution is acidified with 20 c.c. of hydrochloric acid at 25 per cent and dialysed through parchment paper until all the acid is eliminated. The residual colouring-matter is remarkably sensitive. A drop of decinormal alkali produces in 100 c.c. of water mixed with this colouring-matter an instantaneous and sharply marked blue colouration. A drop of a decinormal acid produces an equally sharp change. On precipitating the concentrated solution with alcohol, and drying the precipitate, we obtain a preparation which may be kept for a long time unaltered.

Analysis of Commercial Aluminium.—A. Rössel (*Schweiz. Wochenschrift and Chemiker Zeitung*).—The impurities, chiefly iron and silicon, greatly interfere with the value of the aluminium. The author gradually introduces from 3 to 4 grms. aluminium into about 35 c.c. of hot potassa-lye at from 30 to 40 per cent. The metal dissolves, leaving a black, flocculent residue. It is supersaturated with pure hydrochloric acid in a platinum capsule without previous filtration and evaporated to dusty dryness. The mass is then moistened with hydrochloric acid, and the silica is determined in the ordinary manner. For determining the iron the author also uses from 3 to 5 grms. aluminium, dissolves as above, mixes with an excess of dilute sulphuric acid, heats until the solution is clear, and titrates with permanganate. Great care must be taken that the potassa lye is free from silica.

On Glucinum.—Gerhard Krüss and Hermann Monath (*Ber. Deut. Chem. Gesell.*).—The authors discuss the opening up of glucinum minerals, the preparation of glucina and metallic glucinum, as also the behaviour of glucina as a feeble acid and with feeble acids.

MEETINGS FOR THE WEEK.

TUESDAY, 23rd.—Royal Institution, 3. "The Waterloo Campaign," by E. L. S. Horsburgh, M.A.
Royal Medical and Chirurgical, 8.30.
Photographic, 8.

WEDNESDAY, 24th.—Geological, 8.

THURSDAY, 25th.—Royal Institution, 3. "The Geographical Distribution of Birds," by R. Bowdler Sharpe, LL.D.

Institute of Electrical Engineers, 8.

FRIDAY, 26th.—Royal Institution, 9. "The Imaginative Faculty in its relation to the Drama," by H. Beerbohm Tree.
Physical, 5. "Discussion upon Dr. Lodge's paper, 'The Foundations of Dynamics.'" "A New Photometer," by A. P. Trotter. "Notes on Photography," by Prof. S. P. Thompson, F.R.S. Exhibition of a Vibrating Bar, by G. J. Woodward.

SATURDAY, 27th.—Royal Institution, 3. "Falstaff": a Lyric Comedy by Boito and Verdi, by Dr. A. C. Mackenzie.

ERRATA.—P. 178, in the Table, Series 6, Valence VIII., for "Tr" read "Ir." Also erase the first half of Series 1 and the last half of Series 7.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1748.

ON THE

COMPOSITION OF WATER BY VOLUME.

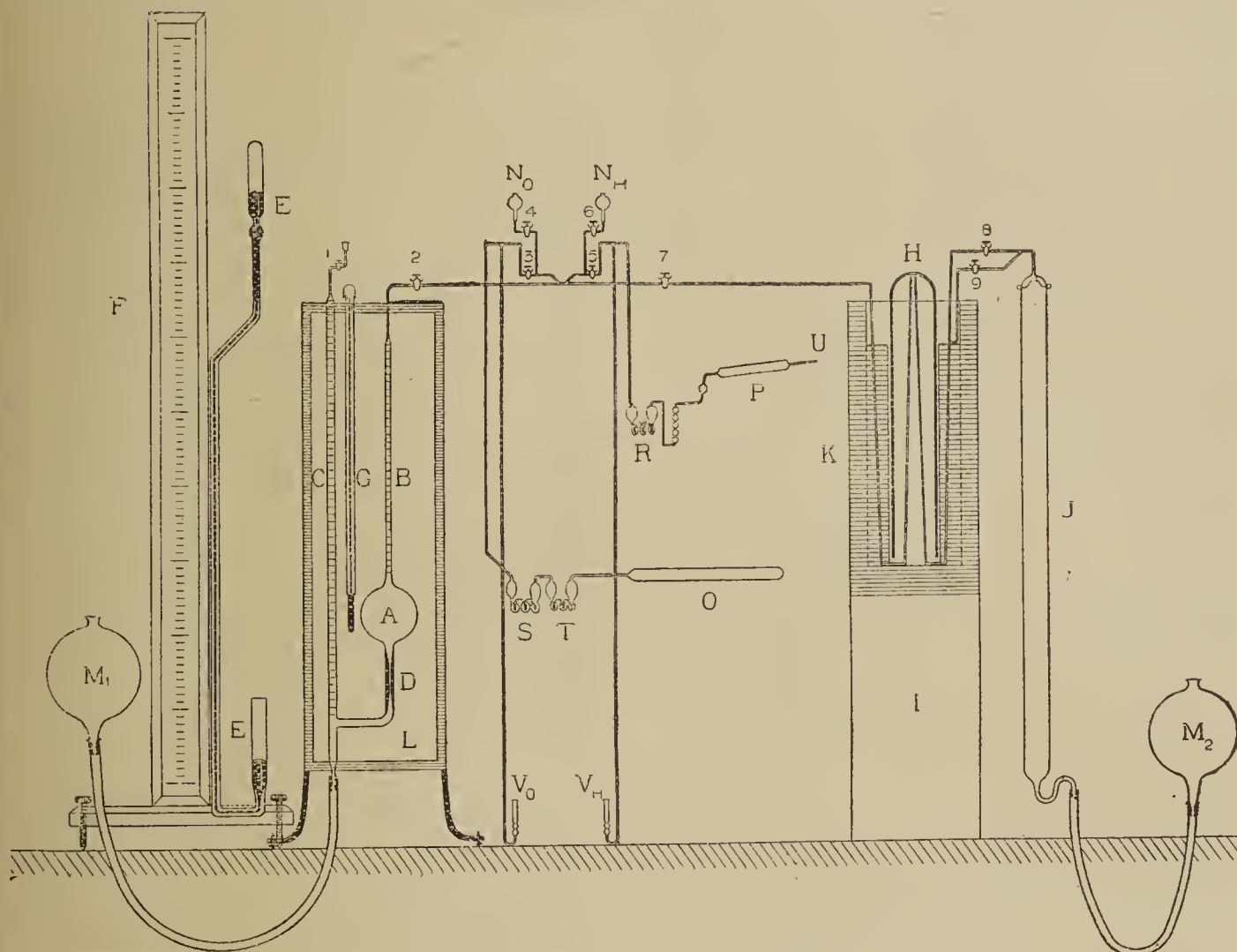
By ALEXANDER SCOTT, M.A., D.Sc.,
Jacksonian Demonstrator in the University of Cambridge.

In a preliminary note presented to the Society in June, 1887, the results of twenty-one experiments on the composition of water by volume were given in detail. The ratio deduced from these experiments was less than two volumes to one of oxygen. This result was unexpected, because of the greater compressibility of oxygen than of hydrogen, but as every one of the experiments pointed to this result, the evidence for it seemed conclusive. Pursuing the investigation with improved apparatus, especially as

measured at constant volume by varying the pressure, which alone, therefore, required measurement in each experiment.

As in the apparatus formerly used, the entire apparatus could be completely exhausted of air before beginning an experiment by using the mercury reservoir (M_1) and the measuring vessel as a Toppler's pump. The gases were measured in A and B, and after measurement were mixed in the jar, H, whence they were drawn into the explosion tube, J, and then exploded in fractions till all was used up. The residue was now passed back into H, and then into B, and there measured, re-transferred to J, and expelled through the tap g into an absorption tube, and analysed with potassium hydrate and pyrogallol for carbon dioxide and oxygen, and for gases not absorbed by these reagents. These gases were most probably nitrogen, hydrogen, and carbon monoxide (from the absorbents). The mixture thus obtained gave at any rate a *maximum* value for any impurity in the gases employed; when it fell below $1/110,000$ the gases were considered pure.

The hydrogen required was made from—



regarded making a complete analysis of the residual gas, a serious source of error was discovered in the use of any combustible lubricant for the taps employed. On substituting syrupy phosphoric acid for the vaseline previously employed, the oxides of carbon disappeared as ordinary impurities. In the latter experiments two forms of apparatus were employed, the chief difference being that in the earlier form the measuring vessel was not of fixed volume, so that both volume and pressure of the gas had to be measured; in the later form the gas was

1. Electrolysis of dilute sulphuric acid.
2. " " hydrochloric acid.
3. Action of steam on sodium.
4. Palladium hydride.

The oxygen was obtained from—

1. Re-crystallised potassium chlorate.
2. Mercuric oxide.
3. Silver oxide.

All the results in which potassium chlorate was used as the source of the oxygen gave low results, doubtless due to traces of chlorine accompanying the oxygen even

after passing through potassium hydrate. The best oxygen was obtained from silver oxide, and the best hydrogen from palladium hydride. The palladium used combined with enough hydrogen to perform twelve experiments in succession. The results of the last series are given in the following Table. The oxygen required was obtained from silver oxide.

Column A contains number of experiment.

" B contains date of experiment.

" C contains measured volume of hydrogen in grms. of mercury.

" D contains measured volume of oxygen in grms. of mercury.

" E contains excess of hydrogen in grms. of mercury.

" F contains excess of oxygen in grms. of mercury.

" G contains impurity in grms. of mercury.

" H contains number of volumes of hydrogen which unite with one of oxygen.

A.	B.	C.	D.	E.	F.	G.	H.
XXV.	Ap. 1	6863.8	3443.8	—	15.4	0.3	2.0020
XXVI.	" 1	6870.0	3432.9	—	2.1	0	2.0024
XXVII.	" 2	6870.1	3439.7	—	9.2	0	2.0026
XXVIII.	" 4	6848.7	3422.1	—	2.9	0	2.0030
XXIX.	" 4	6792.5	3386.6	13.5	—	0	2.0022
XXX.	" 5	6809.2	3399.5	1.5	—	0	2.0025
XXXI.	" 6	6793.9	3399.6	—	7.7	0	2.0029
XXXII.	" 6	6789.6	3389.5	2.9	—	0	2.0023
XXXIII.	" 7	6808.5	3396.4	6.0	—	0	2.0028
XXXIV.	" 8	6793.1	3395.8	—	2.1	0	2.0017
XXXV.	" 8	6786.5	3395.0	—	5.4	0	2.0022
XXXVI.	" 9	6814.8	3411.9	—	9.3	0	2.0028

Mean = 2.00245 ± 0.00007 .

The mean of all the experiments in the variable volume apparatus, and in which potassium chlorate was the chief source of oxygen, is—

2.000903 ± 0.00004 impurity equally distributed in both gases,

1.99925 ± 0.00005 impurity assumed to be all in hydrogen,

in five series of nineteen experiments in all.

The mean of all the experiments in the constant volume apparatus, in which silver oxide was used as the source of the oxygen, and sodium and steam either directly, or after absorption in palladium for the hydrogen, is—

2.002435 ± 0.00006 impurity in both gases equally,
or 2.002431 ± 0.00006 " hydrogen alone.

This is the mean of fifty-three experiments in five series.

If six experiments be rejected we get the value—

2.002466 ± 0.00003

as the result of forty-seven experiments in five series, and any impurity makes no difference, whether it be assumed all in the hydrogen or equally distributed in both gases. The most probable value, however, is 2.00245 .

This value, combined with the value 15.882 for the ratio of the densities found by Lord Rayleigh, gives for the atomic weight of oxygen—

15.862 .

Dittmar and Henderson's value is 15.866

Cooke and Richards's value is 15.869

Leduc (*Comptes Rendus*, cxv., 313) found for the ratio of the volumes, by taking the density of electrolytic gas from strong potassium hydrate solution and his own values for the densities of hydrogen and oxygen,—

2.0037 ,

and for the ratio of densities—

15.905 ,

giving for the atomic weight of oxygen—

15.876 .

Morley's experiments (*Amer. Journ. Sci.*, xli., 220, 276) are objected to on the ground that his apparatus is too complicated, his measuring vessel far too wide for accurate measurement, and to its being used also as the explosion tube, the transferring of his gases from one mercury trough to another, and his giving no means of saturating the gases with aqueous vapour. He further measures his pressures to $1/2000$ th of a m.m. His ratio for the volumes is given as—

2.00023 ,

or only $1/10$ th of the difference from 2.0 exactly of that found by the above-described experiments.

IMPROVEMENTS IN THE MANUFACTURE OF BORAX.

By H. N. WARREN, Research Analyst.

BORACIC, or boric acid, as is well known, is one of the feeblest acids to be met with, being readily replaced by all other known acids, and even in some respects by carbonic acid; but, on the other hand, viewing it as an anhydride, we find it standing foremost, and at elevated temperatures even slowly replacing such acids as phosphoric and sulphuric acids.

Boric anhydride is, in fact, when pure almost entirely fixed at the most elevated temperatures obtainable. A tared platinum crucible containing an ounce of the substance which had been exposed to a full white heat for over two hours, was found after weighing to have lost in weight but 5 grains. The peculiar properties of the acid, however, are vastly different, volatilising readily upon the application of heat, inasmuch that it is practically impossible to distil a solution containing boracic acid without a portion passing into the distillate. Again, if boric acid is melted at a low red heat in a platinum or other suitable vessel, as long as aqueous vapours are discharged, volatilisation of the boron present is perceptible until about 70 per cent of the water present is discharged, the remaining portion of the water being expelled in an almost pure condition.

Taking advantage of these properties, the author has devised a method by which the production of borax is brought about by subjecting common salt (sodium chloride) to the action of the crude boracic acid of commerce aided by superheated steam, the decomposition being effected by employing large clay retorts, composed for the most part of acid resisting material, the tops being tubulated to allow of the introduction of the steam required during the reaction. The retorts being charged with an intimate mixture consisting of well ground salt and boric acid, the neck of the retort being connected with a refrigerator for the purpose of condensing the acid thus obtained.

Directly the retorts assume a low red heat, hydrochloric acid is disengaged in abundance. The heat is now slightly raised, and the supply of steam so regulated that water in the form of steam is allowed to enter through the tubulure in sufficient quantity to condense the hydrochloric acid formed in connection with the refrigerator; the result being a speedy and complete decomposition of the salt employed, with the production of anhydrous borax, which remains in the retorts, whilst a dense and pure acid collects from the condenser.

When the reaction is terminated, the contents of the retorts, consisting of anhydrous borax, is ejected, whilst still red hot, into cold water, where it is allowed to

remain for forty-eights hours, during which time it will have passed into solution, from which, by the ordinary routine of crystallisation, it is obtained as ordinary commercial borax.

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ON THE ABSORPTION-SPECTRA OF SOME COMPOUNDS OF CHROMIUM.*

By W. LAPRAIK, Ph.D., F.I.C.

(Continued from p. 232).

THE substituted chloracetic acids were now used as solvents for chromium hydroxide to see if they also yielded similar absorption-spectra.

The chromium hydroxide was the same as that used in the previous experiments. It was digested with strong aqueous solutions of the acids at the ordinary temperature, and the solutions thus obtained were examined by the spectroscopic as soon as possible, as the acids, under the circumstances of the experiment, are liable to decomposition. The results are not so satisfactory as one would wish, for the absorption-bands are characterised by their indefiniteness, and they are therefore extremely difficult to measure. Another curious characteristic is that these solutions are all of a distinctly blue colour by daylight, although the specimen of chromium hydroxide from which they were made was the same as was used in the fatty acid experiments, in which case the solutions are green. The mono-chloracetic acid solutions are of course decomposed on heating and become green. The absorption-spectrum also alters, and is similar to that given by a solution of chromium hydroxide in glycollic acid. The same is true if the solutions be kept for some time.

The following are the measurements actually obtained by dissolving chromium hydroxide in the following acids.

Monochloracetic Acid (17).—Continuous absorption to 740; shadow to 710; then a very faint band from 698 to 686. The broad absorption from 655 to 504, and continuous absorption from 480.

Dichloracetic Acid (18).—Continuous absorption to 740; shadow to 721; then a very faint indefinite band from 689 to 681. The broad absorption from 655 to 513, and continuous absorption from 480.

Trichloracetic Acid (19).—Continuous absorption to 740; shadow to 714; a very faint indefinite band from 701 to 674. The broad absorption from 655 to 509, and continuous absorption from 480.

These substituted fatty acids, then, do not behave to chromium hydroxide as do the fatty acids themselves, as the absorption-spectra given by the former when they are treated similarly are of an entirely different character. Further, the successive replacement of hydrogen by chlorine appears to move the absorption-band in the red part of spectrum nearer its more refrangible end.

It was thought advisable to compare the spectrum of chromic chloride itself with the above, as it appeared not unlikely that the chloracetic acids might form this compound under the conditions of the experiment, and as it is well known, a solution of chromium chloride gives an indefinite absorption-band in the red part of the spectrum.

Two distinct specimens of chromium chloride were made, as was also a specimen of the colloidal chromic chloride. The same specimen of chromium hydroxide used in the former experiments was dissolved in hydrochloric acid and its absorption-spectrum examined.

Two specimens of chromium chloride were made from the metal.†

(I.) By dissolving the metal in hydrochloric acid.

(II.) The metal was carefully washed with dilute acid for six hours and then washed with water, and the residue dissolved in hydrochloric acid.

All these specimens gave the same absorption-spectrum (29).—Continuous absorption to 717; a very faint indefinite band 704 to 689; a shadow at 653 joining broad absorption from 619 to 550, and continuous absorption from 472.

This absorption-spectrum is very similar to that given by chromium hydroxide dissolved in monochloracetic acid. But it can be shown that the bodies are not identical, for on heating the monochloracetic acid solution—owing to decomposition—it yields a totally different absorption-spectrum, while the chromic chloride is not influenced by heat.

Colloidal Chromium Chloride (30).—This was made in the usual way, by dialysing as neutral a solution as possible of chromic chloride. After some months the colloidal chloride was obtained as a solution of a fine green colour, which could be easily gelatinised on the addition of sodium chloride. The absorption-spectrum of the colloidal solution was similar, but not identical, with that given by the chloride solution. In the case of the colloidal chloride the absorption-band in the red part of the spectrum was distinctly nearer the less refrangible end of the spectrum.

The measurements are as follows:—

Continuous absorption to 800, with a shadow to 750. An indefinite band from 710 to 695. Then a shadow at 665 joining broad absorption from 621 to 544, and continuous absorption from 480. The significance of this absorption-spectrum will be discussed later.

Tribromacetic Acid (20).—Chromium hydroxide is very slightly soluble in a strong aqueous solution of this acid. The absorption-spectrum is similar to that given by trichloracetic acid, but the absorption-band in the red part is moved still nearer the more refrangible end of spectrum. The measurements in a layer of the solution 3 c.m. thick are: Continuous absorption to 770; a faint band from 676 to 668; a shadow at 653 joining the broad absorption at 610 to 534, and continuous absorption from 459.

Glycollic Acid (21).—This acid dissolves chromium hydroxide easily, yielding a solution having a bluish green colour by daylight and a red colour by lamplight. The absorption-spectrum is as follows:—

Continuous absorption to 758. Then two bands in the red 723 to 714, and 706 to 695 respectively. Then a sharp shadow at 670, which joins the broad absorption from 644 to 507, and continuous absorption from 473.

Lactic Acid (22).—This acid easily dissolves the chromium hydroxide. The solution was green by daylight and red by lamplight. The absorption-spectrum given was similar in character to that given by the preceding acid.

The absorption-bands are very indefinite, and their edges indistinct, so that the same difficulty in measuring them was experienced. The absorption-spectrum is as follows:—Continuous absorption to 770. Two very faint and indistinct bands at 721 and 707 respectively. Then a somewhat more definite and broader band at 676—665. Then the broad absorption from 629 to 533, and continuous absorption from 467.

The bands 721 and 707 seemed to be moved towards the less refrangible end of the spectrum than is the case in glycollic acid. But the apparent movement is slight, and the bands indistinct, so that it is impossible to speak with certainty.

Trichlorolactic Acid (23).—A saturated solution in cold water was made of this acid, and the chromium hydroxide dissolved in the cold in it. The solution was red by daylight as well as by lamplight. The absorption-bands in this case are also very indistinct, but after repeated measurement they appear to be as follows:—Continuous absorption to 721. Two faint bands at 710 and 674

* *Journ. für Prakt. Chemie*, xlvii., 305 (1893).

† Obtained from E. Merck, Darmstadt.

respectively. A shadow at 655 joining broad absorption from 610 to 526, and continuous absorption from 483.

These measurements point to the absorption-bands being moved slightly towards the red end of the spectrum as compared with lactic acid.

Phosphoric Acid (24).—Chromium hydroxide was dissolved in an excess of this acid, producing a fine green coloured solution, which gave an absorption-spectrum which is somewhat remarkable. It is as follows:—Continuous absorption to 740. Then a band in the midst of partial absorption at 698–686. Then a space free from partial absorption. Then a band at 670–650, another band at 639–621 and partial absorption to 585, and finally continuous absorption from 471.

The notable point of this absorption-spectrum is that there is so little absorption in the green part. In this respect the phosphoric acid solution is different from all the other salts of chromium examined, with one exception, potassium chromicyanide.

Malic Acid (25).—A strong aqueous solution of this acid easily dissolves chromium hydroxide. The solution is bluish-red by daylight and red by lamplight, and gives the following absorption spectrum.

Continuous absorption to 729. Then a band at 707 to 695. A deep shadow at 670 which joins the broad absorption at 644 which ends at 498, and continuous absorption at 480.

Tartaric Acid (26).—The absorption-spectrum of a solution of chromium hydroxide in this acid is known, as it has been mapped by Th. Erhard (*loc. cit.*).

My measurements are:—Continuous absorption to 800. A very indefinite band at 707–695. A shadow at 668 which joins the broad absorption at 639 which ends at 501, and continuous absorption from 475.

Citric Acid (27).—A strong aqueous solution of this acid, when used as a solvent for chromium hydroxide, gives an absorption-spectrum very similar in character to that given by the two previous acids. The following were the measurements obtained:—

Continuous absorption to 736. A faint band at 707 to 698. A shadow at 660, which joins the broad absorption at 629, and which ends at 504. Then continuous absorption from 467.

Isethionic Acid (28).—A 50 per cent aqueous solution of this acid was used to dissolve chromium hydroxide, which it did without difficulty. The colour of the solution was bluish green by daylight and red by lamplight. The absorption-spectrum was as follows:—

Continuous absorption to 717. A very indefinite band at 695–668. The broad absorption at 653–506, and continuous absorption from 480.

The absorption-spectra of the foregoing acids are characterised by the indefiniteness of the absorption-bands in the less refrangible parts, and they fade off so gradually on both sides that it is extremely difficult to measure them.

The close resemblance of these absorption-spectra, together with the great differences of molecular complexity of the acids used as solvents, suggested the probability of the absorption-spectra given being produced mainly by chromium hydroxide or oxide, and not to the combination of this body with the acids used as solvents.

It is well known that chromium hydroxide is not precipitated by caustic alkalis in presence of certain organic bodies, as sugar, tartaric acid, &c. Some experiments were made with this view. Solutions of chromium hydroxide in citric and tartaric acids were made, and a slight excess of caustic potash was added, and the absorption-spectrum observed. These solutions gave the same absorption-spectrum, which is as follows:—

Continuous absorption to 721. A faint band at 710 to 692. A shadow at 665 joins the broad absorption at 617, which ends at 547. And continuous absorption from 473. Ammonia solution was substituted for caustic potash, but the resulting absorption-spectrum was the same as the above.

In another set of experiments the chromium salt was varied; chromium chloride and sulphate were used together with strong aqueous solutions of cane sugar, glycerin, and tartaric acid respectively. Slight excess of caustic potash was added in one case, and an excess of ammonia solution in the other. The absorption-spectra in all these cases did not differ from the one given last.

Chromium hydroxide itself dissolves in an excess of caustic potash; this also gave the same absorption-spectrum as the above, and, lastly, freshly precipitated chromium hydroxide, precipitated by caustic potash and suspended in water, gave exactly the same absorption-spectrum (31).

There can be no doubt, then, but that the above is the absorption-spectrum given by chromium hydroxide, and as was to be expected it agrees exactly with that given by a solution of colloidal chromium chloride, and also fairly well with the absorption-spectra given by citric, tartaric, and malic acids.

It would therefore seem probable that in these cases and probably in others the acids have no power in modifying the absorption-spectra, which therefore must be produced either by chromium hydroxide or oxide existing in the various solutions examined.*

It is further to be noticed that the band 710–692 of chromium hydroxide is represented in most of the chromium salts examined; a glance at Table I., column 2, will render this evident. Sometimes it occurs as a broad band, as in the case of chromium chloride; sometimes as a faint, thin, incidental band, as in the fatty acid series; and sometimes as a thin, sharp, and exceedingly dark band, as in the case of the chromoxalates; while in the substituted chlor-acetic acids it is somewhat moved towards the more refrangible end of the spectrum.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.†

FIRST PAPER: THE ANALYSIS OF BARIC BROMIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 233).

The Choice of Material.

It has been already stated that the most satisfactory determinations of the atomic weight of barium have had baric chloride as a starting point. In many respects this substance is well adapted for the purpose; but one serious cause of error must be carefully guarded against in the usual method adopted for its analysis. The well-known solubility of argentic chloride influences the accuracy, not only of the weight of chloride obtained, but also of the apparent end point of the precipitation after the method of Gay Lussac. Long ago Stas‡ pointed out this cause of error, and carefully described his method of procedure, that others might correct his results if they were found to be based upon an incorrect assumption. He added an excess of silver to the chloride to be investigated, and then added the standard solution of a chloride until no more cloudiness was observable. Such a method under ordinary circumstances requires from two to eight m. grms. less of silver to correspond with a given weight of chloride than would be required if the solutions were added in the inverse order.

* Since the above work was done, Recoura (*Comptes Rendus*, cxii., 1439) has shown by thermic methods that a green basic sulphate— $2\text{Cr}_2\text{O}_3 \cdot 5\text{SO}_3$ —exists in solution when the blue sulphate is converted by heating into the green salt, and also that this salt is unable to fix a further quantity of acid.

† *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

‡ Aronstein's translation of Stas's Memoir, pp. 46, 56, 59, and especially 295 (Leipzig, 1867).

A number of years afterward* Stas changed his method of procedure, and selected the point half-way between the two extremes as the true end point of the silver reaction. He gave reasons for this change of view, but wholly ignored his previous results. Commentators have laid hardly enough stress upon this important difference between the two series of determinations, although it necessarily involves an error in one series or the other.

Working before even the earliest date of Stas's publication upon this subject, the experimenters upon the atomic weight of barium naturally overlooked the whole question. As nearly as may be guessed from their incomplete accounts, they usually selected the end point obtained by gradually adding argentic nitrate to baric chloride; hence their results cannot be compared with either of Stas's series.

Much time during the past eighteen months has been spent upon this question. The investigation of baric chloride showed that results for the atomic weight of barium varying from 137.35 to 137.50 might easily be obtained from the purest possible salt, according to the interpretation of the data. At last a definite conclusion was reached, and the work is now nearly ready for publication.

The necessity for some other basis for the atomic weight of barium early led to the search for a new starting point. In the course of this search most of the available baric salts were investigated with regard to their adaptability for the present purpose.

Baric nitrate holds water with great obstinacy, and no certain point of constant weight could be reached by gradually heating it. Besides, the only two methods available for its analysis are extremely unsatisfactory. The conversion into the chloride is rendered very difficult because of the insolubility of both the nitrate and chloride in strong acids. The complete conversion of the nitrate into the sulphate is also difficult, because of the well-known occlusion of one salt by the other. Moreover, supposing the analysis by either method to have been satisfactorily performed, the data furnished would give only the worst possible foundation for the calculation of the atomic weight of barium (see Ostwald, *Allgemein. Chem.*, i., 23). Many qualitative and quantitative experiments led to the complete rejection of baric nitrate as the material for analysis.

Baric bromate is very readily prepared in a pure state by a few successive crystallisations, and it was hoped that this salt would furnish especially valuable testimony upon the case. But investigation showed that it was impossible to be certain that the crystallised salt did not contain an excess of occluded water. Upon the other hand, it is doubtful if all the water of crystallisation can be expelled without a slight decomposition of the salt. Since water is the one impurity most to be dreaded in all such work, baric bromate was rejected, except as a means of obtaining the bromide in a pure state.

The carbonate was next experimented upon, and, while the results were more promising than those from the nitrate and bromate, they were less satisfactory and conclusive than those obtained from baric bromide.

The advantages of the use of a bromide for an investigation upon atomic weights are so manifest, and have been so often discussed, as to need no further mention. The current descriptions of the deliquescence and instability of the baric salt alone postponed the consideration of this substance. Investigation showed that misleading statements about the salt have found their way into chemical literature. In reality, the substance is as well adapted for accurate work as baric chloride and most other materials upon which we must rely.

(To be continued.)

* The Memoir was presented in 1876, according to the title page. *Mem. de l'Acad. de Belg.*, Nouv. Ser., xliii. See also Van der Plaats, *CHEM. NEWS*, liv., 52, 88.

THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Continued from p. 177).

PARRY determines the small percentage of carbon in very soft steels by the method of combustion in vacuum. The dry carbonaceous residue obtained by any of the usual methods, *i.e.*, by digestion with copper sulphate or chloride, &c., is mixed with excess of pure copper oxide, previously ignited in a vacuum to remove all gaseous matter and moisture. The moisture is transferred to a porcelain tube closed at the end, and the tube nearly filled with copper oxide. The tube, &c., is attached to the Sprengel mercury air pump, exhausted, and allowed to stand for one hour; if no leakage occurs, a full red heat is applied by any convenient means—preferably a small gas combustion apparatus—for one hour. Carbonic acid is freely evolved, and is pumped into a tube graduated in 1-10th c.c. attached to the pump. The gas is accurately measured with the usual precautions, and the percentage of carbon calculated therefrom.

Very close results may thus be obtained, and a very minute quantity of carbon may be estimated with certainty. (For details and full description of apparatus see Blair's iron and steel analysis). This method at first sight may seem too elaborate and complicated for ordinary work, but our experience is to the contrary. Once the apparatus is in complete working order, combustion may be made with great facility. The same tube and copper oxide may be used repeatedly if the precaution be taken of keeping the tube, &c., always attached to the pump, and slightly heating and pumping just previous to use.

Graphite.

For the determination of this constituent four or five grms. of the metal are dissolved with the aid of a gentle heat in hydrochloric acid, the residue collected on an asbestos filter similar to that employed for the collection of the carbonaceous residue in the estimation of total carbon, washed with hot water, a solution of caustic potash, alcohol, and a little ether. The residue is then dried, mixed with copper oxide, burnt in a stream of oxygen,† the resulting carbonic acid being collected and weighed.

This method furnishes very accurate results, but is rarely employed, the graphite being determined either in the case of silicon previously dealt with, or preferably by the method now described, which yields results sufficiently accurate for all technical purposes. Five grms. of the sample, contained in a beaker, are digested at a gentle heat, with 60 c.c. of dilute hydrochloric acid, and when the solution is nearly complete, 20 c.c. of the strong acid is added and further digested. Dilute the resulting solution with a large volume of water, collect the residue composed of graphite, &c., on a weighed filter paper, wash well with water, a dilute solution of hydrochloric acid, and a solution of caustic potash, to remove silicon, and finally to remove hydrocarbons, with alcohol and ether. The filter paper and contents are then transferred to a water oven, dried at 100–120° C., and weighed. As the graphite thus obtained may still contain small quantities of silicon, &c., in the form of slag, it is placed in a platinum crucible, ignited at a strong heat, the residue weighed and deducted from the original weight of the graphite, and if required the percentage of slag thus obtained tabulated. Analysts do not usually give determinations of slag and diffused iron oxide, but even for practical work these should always be estimated.

Sulphur.

The methods employed for the determination of sulphur in iron and steel are based upon two principles, *viz.* :—

* From *Industries*, April 4, 1893.

† For a description of the apparatus employed and manner of carrying out the combustion consult a work on organic chemistry.

(1) That upon treating the metal with an oxidising reagent, such as nitric acid or other oxidiser, the sulphur is oxidised into sulphuric acid, which is subsequently precipitated as barium sulphate (BaSO_4) with barium chloride. (2) The sulphur is evolved as sulphuretted hydrogen upon treating the iron or steel with sulphuric or hydrochloric acid. Of the two, we are of opinion that the method based upon principle (1) yields, in the hands of a skilful operator who rigidly observes the necessary precautions, the most accurate results, and, furthermore, that those obtained by the other methods should be checked by it.

The *modus operandi* of the method is as follows:—The filtrate contained in a beaker, remaining from the estimation of the silicon, or, if it has not been determined, that obtained upon dissolving 4 grms. (with sulphurous iron 2 or even 1 grm. is quite sufficient) of the sample in 60 c.c. of nitro-hydrochloric acid, with subsequent evaporation of the solution to complete dryness, re-dissolving in hydrochloric acid, and separation of the silica as previously described, is gently evaporated down to dryness. The beaker, &c., is allowed to cool, the contents moistened with a small quantity of hydrochloric acid, a gentle heat applied, and the solution again taken to dryness.

This operation is repeated until it is judged that the whole of the nitric acid is expelled. Finally, a small quantity of hydrochloric acid is added to the dry residue, and the solution evaporated until a crust commences to form on the surface, at which point it is arrested and the crust dissolved in three or four drops of hydrochloric acid. If these directions be strictly carried out, the solution will be free from nitric acid and nitrates, which are precipitated by barium chloride, as also from an excess of hydrochloric acid, which is essential for the obtainment of good results, barium sulphate being in our experience soluble to a slight extent in acid solutions of ferric chloride. The solution thus obtained is diluted with 700 c.c. of water, and the sulphuric acid contained in the same precipitated as barium sulphate (BaSO_4) by the addition of 5 c.c. of barium chloride (prepared by dissolving one part of the crystals in ten of water). After thoroughly mixing the solutions, cover the mouth of the beaker with a watch-glass and set aside to stand in a warm place for at least twelve hours, during which time the barium sulphate will be precipitated. At the expiration of that time syphon off as much as possible of the clear supernatant liquid, and throw the remainder, together with precipitate—removing the portions adhering to the sides, &c., of the beaker—on to a Swedish filter. Wash the filter and contents two or three times with a dilute solution of hydrochloric acid and thoroughly with hot water, transfer filter, &c., to a platinum or porcelain crucible, ignite at a bright heat, and when cold weigh the residual BaSO_4 , every hundred parts of which correspond to 13.73 parts of sulphur.*

It occasionally happens that the precipitate, instead of being perfectly white, is of a pinkish tinge, due to the presence of iron, but the quantity is so small that it may be safely disregarded. If, however, it is a decided red, the precipitate contained in a platinum crucible is fused with six times its weight of sodium carbonate, the fused mass treated with a small quantity of dilute hydrochloric acid, the solution filtered, and the barium sulphate, now free from impurities, collected on a filter, washed, &c.

The methods based upon principle (2) are numerous, the majority being rapid and of easy execution. These advantages are, however, considerably lessened by the fact that they cannot be said to furnish absolutely accurate results on account of the probability of a proto-sulphate being retained in solution, likewise the insoluble matter in some irons seems to retain small quantities of sulphur. Neither can they be employed with all classes of iron, such as white iron. Where only approximate results are

desired they furnish very fair results in a short time. In the method now described a metal is precipitated as sulphide from the solution of its salts by conducting the sulphuretted hydrogen evolved through. The absorbent employed is a solution of copper sulphate, prepared by dissolving 60 grms. of the crystals in a litre of water.

The details of the method are as follows:—In a small glass flask, A (Fig. 2), provided with a caoutchouc cork, through which a safety acid funnel, B, passes, reaching to nearly the bottom of the flask, and a tube, C, bent at right angles, welded to the neck, place 4 grms. of the sample, and in the glass cylinder, D, of 250 c.c. capacity, 220 c.c. of the copper sulphate solution. Arrange the apparatus over a gas-burner so that the tube, C, reaches inside nearly to the bottom of cylinder D, and through the funnel pour in some dilute sulphuric acid (one part acid to three of water) until the stem is immersed to a

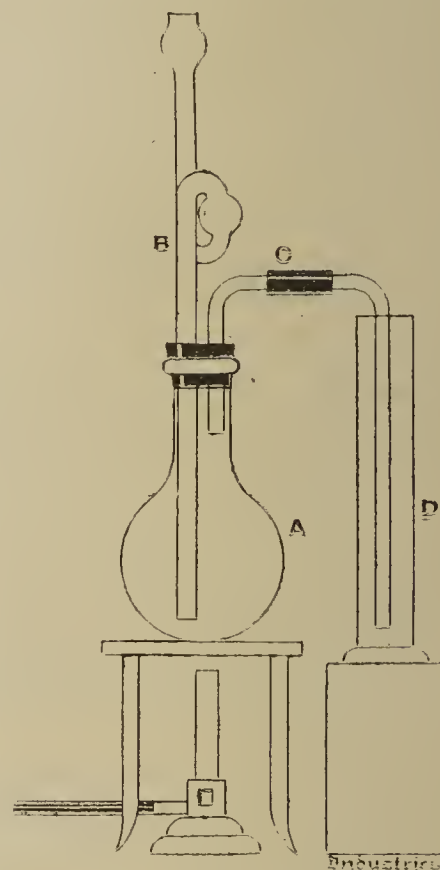


FIG. 2.

depth of half-an-inch. The acid immediately attacks the metal with evolution of sulphuretted hydrogen, &c., which makes its escape through the tube C into the copper sulphate, where as it ascends it is decomposed, the sulphur combining with the copper, forming a precipitate of copper sulphide (CuS), while the hydrogen is liberated. Towards the end, when the reaction becomes enfeebled, accelerate by applying a gentle heat under the flask. When all action is at an end, expel the gas remaining in the flask by pouring in through the funnel lukewarm water, taking care that it does not overflow into the copper sulphate solution. Remove A, rinsing into D any portions of the precipitate which may adhere to the stem of C, collect the precipitate on a filter, wash thoroughly with cold water, and convert into copper oxide (CuO) by ignition at a red heat, and weigh. The ignited precipitate of copper sulphide contains 40 per cent sulphur.

(To be continued).

Production of the Sodium Light.—H. Král (*Chem. Zeitung*).—The author uses asbestos rods saturated with common salt and prepared from asbestos paper. They are saturated by steeping in brine, and drying.

* The principal objection to this method is that it is almost impossible to obtain HNO_3 and HCl acids free from SO_4 .

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 4th, 1893.

Dr. ARMSTRONG, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. John Bateman, Saltney, near Chester; Robert S. Cahill, 90, Park Lane, Norwich; Alexander Mitchell Martin, Douglas Villa, Dunbeth Road, Coatbridge; Charles Alexander McKerrow, 41, Eccles Old Road, Pendleton, Manchester; William Ridgely Orndorff, Ithaca, N.Y., U.S.A.; Wilfred Sessions, Russell House, Gloucester; Frank Ernest Thompson, 97, Murdock Road, Handsworth, Birmingham.

In answer to a question put by Mr. Cassal, the PRESIDENT expressed the opinion that to read the certificates of some without reading those of all candidates would be to make an invidious distinction, and that, therefore, if such a request were made, he should rule that it was out of order.

The following candidates were duly elected Fellows of the Society:—John Frederick Briggs, Julian L. Baker, William A. Bone, Laurence Augustus Baine, John Chas. Burnham, William Robert Burnett, Joshua Buchanan, Ralph Edward Brown, George Clayton, James Cameron, Harry Williamson Dixon, H. W. Dickinson, Robert Cecil Turle Evans, Thomas Edwards, Alfred Roland Gower, Robert George Grimwood, John Addyman Gardner, Hedley Gordon Jones, Hooper Albert Dickinson Jowett, Sorabji Manekji Kaka, Edmund George Lamb, Herbert Lloyd, Alan E. Munby, Henry John Monson, John Alan Murray, J. Frank McGregory, A.B., A.M., James Mason, Raffaello Nasini, William Henry Oates, S. Parrish, William Rintoul, James Henry Robbins, George Rudd Thompson, Frank P. Vandenbergh, B.S., M.D., A. F. Watson, John Wilkinson.

Of the following papers those marked * were read:—

*II. "The Hydrates of Sodium, Potassium, and Lithium Hydroxides." By S. U. PICKERING.

By cooling solutions of sodium hydroxide the author has succeeded in isolating a large number of hydrates in the solid crystalline condition. They considerably outnumber those of which he obtained indications by means of changes of curvature in the case of sulphuric acid—comparing similar ranges of strengths in the two cases—and hence no improbability can any longer be held to attach to these latter on account of their being so numerous.

The formula of the various hydrates isolated and their freezing points are as follows:—

	Freezing-point.
NaOH·H ₂ O	64.3°
NaOH·2H ₂ O	12.5
NaOH·3.11H ₂ O	2.73°
NaOH·3.5H ₂ O	15.55
αNaOH·4H ₂ O	7.57
βNaOH·4H ₂ O	— 1.70
NaOH·5H ₂ O	— 12.22
NaOH·7H ₂ O	— 23.51

The freezing-points or solubility curves of all these hydrates have been followed throughout considerable ranges; several of them—in one case as many as four—overlap each other. As it is scarcely possible to conceive that a crystalline hydrate can be extracted from a solution unless some molecules of that hydrate are present in the solution, this fact must prove that in some cases as many as four, probably even more, different hydrates exist in the same solution.

The existence of two different tetrahydrates is noticeable, as also is that of the complex hydrate of the formula

NaOH·3.11H₂O, or NaOH·3H₂O + NaOH·4H₂O, which is similar to two of the hydrates of which the author obtained indications in the case of sulphuric acid. Of the eight hydrates, that containing 3½ molecular proportions of water is the only one which has been previously described.

In the case of potassium hydroxide, two new hydrates—a mono- and a tetra-hydrate—have been isolated and examined, in addition to the already known dihydrate. The freezing-points of these are—

	Freezing-point.
KOH·H ₂ O	143°
KOH·2H ₂ O	35.5°
KOH·4H ₂ O	— 32.7

In the case of lithium hydroxide, the already known monohydrate was the only one obtained.

12. "Detection of Arsenic in Alkaline Solutions." By JOHN CLARK, Ph.D.

The author shortly reviews the different methods by which arseniuretted hydrogen is generated in an alkaline solution, and finds, as pointed out by Hager, that Fleitmann's process, which depends on the interaction of finely-divided zinc and caustic potash, does not detect arsenic acid, but he is unable to confirm the statement of H. Fresenius, that Gatehouse's modification of Fleitmann's test indicates arsenic acid, as he has not been able to volatilise the slightest trace of arsenic by heating arsenate of soda with a large excess of pure aluminium and caustic soda, and he attributes the results obtained by Fresenius to the use of impure aluminium, or to the presence of arsenious acid in the arsenic acid. Experiments made to test the applicability of the Gatehouse process in estimating arsenic seem to show that, although it is very delicate and very convenient, it does give quantitative results, even when the whole of the arsenic is in the form of arsenious acid. He also finds that arsenic acid in an alkaline solution resists the action of sodium amalgam, and he concludes, therefore, that none of the methods which have been proposed for the generation of arseniuretted hydrogen in an alkaline solution detect arsenic acid.

13. "Improvements in Reinsch's Process." By JOHN CLARK, Ph.D.

Reinsch's process, as carried out in the ordinary way, is capable of demonstrating the presence of very minute quantities of arsenic, and, according to Letheby, it withdraws every, and the smallest, trace of arsenic from organic mixtures, but there are two objections to its use in medico-legal cases.

1. When the quantity of arsenic is small, a stain is obtained which it is sometimes difficult to identify as arsenic, because the coated copper when heated is apt to give a layer of chloride of copper and organic matter, instead of arsenious acid.

2. It is not suitable for the quantitative estimation of arsenic, as it is not possible by means of heat to volatilise the whole of the arsenic from the copper.

The author's improvements consist in identifying the arsenic or antimony on the copper with greater certainty, and at the same time estimating the amount of each when they occur together. For this purpose he digests the coated copper in a cold mixture of dilute caustic potash and peroxide of hydrogen, which dissolves the arsenic and antimony, and converts them into arsenate and antimonate of potassium. The solution is then boiled, filtered, to get rid of the oxide of copper, evaporated to small bulk, and distilled with ferrous chloride and strong chlorhydric acid. The distillate is then saturated with sulphuretted hydrogen, and the arsenic weighed as sulphide, after being freed from traces of sulphur by washing with carbon bisulphide and alcohol. The residual liquid, from which the arsenic has been thus removed by distillation, is then tested for antimony.

DISCUSSION.

Dr. BERNARD DYER drew attention to a remarkable difference in the results obtained on testing for arsenic by Marsh's process when the zinc used was in the shape of rods instead of being granulated. Some time since he had detected arsenic, not a mere trace, but a tangible, weighable quantity, in a certain pigment; but his results were disputed by the maker of the colour, who stated that a test made with rigid precautions by another operator had afforded no evidence of the presence of arsenic. The speaker had therefore met the other operator, and the following very curious results were obtained:—An ounce or two of his (Dr. Dyer's) highly purified granulated zinc was introduced into the Marsh apparatus, together with pure chlorhydric acid; at the end of an hour no appreciable deposit was formed in the heated tube, but on introducing 2 grms. of the pigment a dense arsenical mirror was soon obtained. The apparatus was then washed out, and charged with cast rod zinc, brought by the challenging operator; not only, however, was no deposit formed in the tube during the blank trial, but also on introducing 2 grms. of the pigment, no indication of the presence of arsenic was obtained, although the experiment was continued during an hour. Further experiments were made with this cast zinc, in which arsenious acid was deliberately added; when small fractions of a m.grm. were taken, and gas was slowly evolved, the arsenic was almost completely held back, and was but very partially deposited even when several m.grms. were taken, the results being altogether different from those obtained on using the granulated zinc. A number of samples of cast zinc were found to behave similarly. He had no doubt that some condition, probably of a physical kind, prevailed in cast zinc that did not prevail in the case of granulated zinc. The matter required further investigation, as it was one of obvious importance in toxicological work. There was little doubt that the arsenic is precipitated in the generating-bottle. Even granulated zinc produces some precipitation. It has been already shown that the frequently advocated use of platinum in the generating-bottle tends to hold back arsenic, and it seems probable that some couple may be formed in cast zinc.

*14. "*The Action of Light in Preventing Putrefractive Decomposition and in Inducing the Formation of Hydrogen Peroxide in Organic Liquids.*" By ARTHUR RICHARDSON, Ph.D.

It was shown in 1878 by Downes and Blunt (*Proc. Roy. Soc.*, xxvi., 488) that the development of bacteria and other putrefractive organisms is arrested under the influence of sunlight and oxygen; Janowski, Buchner, and Marshall Ward have recently made observations of a similar character. This sterilising influence of light in presence of oxygen has apparently always been regarded as the outcome of an action exercised within the organism; the author describes a number of experiments with urine, made with the object of ascertaining whether, when sterilisation has been effected by light, any oxidising agent, such as hydrogen peroxide, is formed, and whether such substance may not be the sterilising agent.

The method of testing is fully described, reliance being chiefly placed on the production of a yellow colour on the addition of a solution of titanous oxide in sulphuric acid; it is shown that this test affords a means of accurately estimating small amounts of hydrogen peroxide.

The author finds that, although no hydrogen peroxide is formed by the action of oxygen on sterilised urine in the dark, an appreciable amount is formed on exposing such urine to light, which is a proof that the production of the peroxide is not dependent on the presence of organisms. Urine in which bacteria have once flourished and which has then been sterilised at 100° no longer gives hydrogen peroxide on insolation.

Substances which destroy hydrogen peroxide were found to facilitate growth; thus, two portions of sterilised

urine were exposed to light during several days, and to one of them was added a quantity of sterilised manganese dioxide; both were then placed in a dark cupboard: whereas both originally contained hydrogen peroxide, after twenty-four hours that to which no manganese peroxide had been added alone gave the yellow colour with titanous acid; and after fourteen days, fungoid growths had developed in the liquid containing manganese peroxide, while the other portion was still clear and contained hydrogen peroxide.

Experiments are described showing that if peroxide of hydrogen be added to fresh urine, this may be kept during a considerable period in the dark without the peroxide being entirely decomposed, and that its presence renders the liquid much less prone to undergo change under the influence of organisms, while, if added to urine in which fermentative change has already set in, it is rapidly decomposed.

15. "*The Supposed Saponification of Linseed Oil by Dutch White Lead.*" By J. B. HANNAY, F.R.S.E., and ARTHUR E. LEIGHTON.

Statements are quoted from technical writers showing the existence of a belief that white lead acts on the oil in which it is ground, and even indicating that the heat given out in mixing the pigment with oil is due to the occurrence of an interaction. The authors show that no heat is given out on mixing oil and white lead without undue friction, and that the heat observed in manufacturing operations is due to the conversion of the energy of the engine into heat by friction.

Also that white lead can be freed from oil as readily as any other pigment if a sufficient quantity be used, but it requires 100 c.c. to every grm. of pigment to effect a complete separation. Oleate of lead, whether basic, neutral, or acid, is shown to be readily soluble in ether, and it was mixed with white lead, both dry and ground in oil, and then extracted with ether, thus proving that if present it would certainly dissolve in the ether used to extract the oil. The method of testing is described, and it is shown that by passing sulphuretted hydrogen through the ethereal solution of the oleate, the faintest trace of oleate can be detected.

A series of tests carried out on samples of Dutch white lead produced by the most eminent makers is then described, and it is shown that no trace of oleate is present in any of them, nor does any insoluble organic compound cling to the lead after the oil is extracted. It is shown that normal carbonate of lead dissolves in heated oil more readily than hydrate, and that the hydrate is actually less acted upon at high temperatures than either Dutch white lead or normal carbonate, so that the hydrate does not saponify the oil.

It is shown that so small a quantity as 0.01 of oleate will seriously darken white lead when exposed to the air, and in presence of diluted sulphuretted hydrogen the smallest quantity of oleate causes the paint to darken when the pure white lead retains its colour, showing that the formation of a lead oleate would be deleterious.

DISCUSSION.

Mr. HARLAND remarked that evidence of an action between linseed oil and white lead was to be found in the fact that it was impossible to wholly remove the oil from an ordinary white lead paint by means of ether.

Mr. BERTRAM BLOUNT said that the action between the linseed oil and white lead did not result in the saponification but in the oxidation of the oil, one of the products being "linoxin," which, though soluble in alcohol, was scarcely soluble in ether. This explained the fact alluded to by Mr. Harland. He took exception to Mr. Hannay's experiments, on the ground that he had used lead oleate, and not the lead linoleate which would result if any "saponification" occurred in linseed oil.

Mr. W. F. REID drew attention to the work of Mulder and Pettenkofer, which showed that no "saponification" was effected by dry white lead. It appeared that the

white lead promoted slow oxidation of the oil and not "saponification."

The PRESIDENT said that he failed to understand the author's object in bringing such a communication under the notice of the Society. The statements made by the writers referred to could scarcely be taken seriously; such men would probably be unable to explain what "saponification" meant. No chemist would suppose that carefully dried white lead and oil, such as the authors used, would interact when carefully mixed, or that even carefully dried caustic soda would act under such conditions. It was apparently the universal belief that Dutch white lead had certain peculiar properties, but its effect was undoubtedly a complex one, in which probably not only the white lead and oil played a part, but also moisture, air, light, and time.

In reply, Mr. HANNAY said that his experiments were made to refute the statement made in several technical manuals on paints.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, May 12th, 1893.

Prof. A. W. RÜCKER, F.R.S., President, in the Chair.

A PAPER on the "*Drawing of Curves by their Curvature*" by C. V. BOYS, A.R.S.M., F.R.S., was read, and demonstrations of the method employed given.

Whilst giving a course of lectures on Capillarity in 1891, the author wished to explain the principles upon which the form of a water-drop depended; and finding Lord Kelvin's rule (*Proc. Roy. Inst.*, January 29, 1886) cumbersome, devised the modification now described. To apply Lord Kelvin's rule for drawing the generating curve of a capillary surface of revolution, the values of the expression—

$$\left(\frac{\delta}{a^2} + \frac{1}{OP} + \frac{1}{NP} - \frac{1}{N'P'} \right) - 1,$$

where PP' is a short arc of a circle with centre O, N and N' the points on the axis of revolution in which the lines OP and OP' cut it, δ is the difference of level between P and P', and a a linear parameter, have to be calculated. Compasses are then set to this length, and another short arc, P'P'', drawn with centre O' on the line P'N', and the process repeated. This construction depends on the fact that the total curvature—

$$\left(\frac{1}{OP} + \frac{1}{NP} \right)$$

is proportional to the hydrostatic pressure at the point P, i.e., proportional to the depth below the plane surface of the liquid. To avoid the trouble of finding reciprocals, a rule was divided so that the distance from what would be the zero of the scale are the reciprocals of the numbers attached to them, and the curvature of an arc, being the reciprocal of its radius, can be read off immediately by the rule. To meet cases where the curvatures of surfaces are in opposite directions, the zero, or ∞ , is put at the middle of the rule and divided both ways.

The chief gain depends on the abolition of cumulative errors due to compass settings, which is effected as follows:—The rule is made of a thin slip of transparent celluloid with a small hole at the centre, or ∞ . A small brass tripod, with needle feet, is placed so that two feet just penetrate the paper, and the third rests on the longitudinal straight line of the strip, which passes through the centre hole, thus forming a temporary but rigid centre about which the rule can rotate. A pen or pencil through the hole at ∞ traces out an arc whose curvature is equal to the reading of the scale where the needle point presses. When the rule crosses the axis of rotation of a generating curve, the numbers representing both curvatures are

visible, and the position of the needle point corresponding to a given total curvature can readily be found. A small arc is then drawn. Holding the strip firmly on the paper the tripod is moved a little, so that the sum of the two readings at the needle point, and where the rule crosses the axis, has the value corresponding to the position of the tracing-point, and another arc drawn. Repeating the process a very perfect and accurate curve results. Details for drawing nodoids, unduloids, catenoids, and other curves, are given in the paper, and many beautiful examples which had been executed by Miss Stevenson were exhibited at the meeting. The author also pointed out that the locus of points about which the strip successively turns, is the evolute of the curve drawn by the tracing-point.

Prof. PERRY considered the method a new departure of great value. When he (Prof. Perry) drew the capillary surfaces of revolution in 1875, he found that cumulative errors produced considerable discrepancies.

Prof. HENRICI thought the method would be a very useful one.

Prof. GREENHILL said one would now be able to secure better diagrams of transcendental and other curves than heretofore, and he thought Mr. Boys' method would supplant the laborious processes now used to determine the paths of projectiles. When the resistance varied as the square of the velocity, the elevation for maximum range depended on the initial velocity, and for a cube law, both elevation and range tend to finite limits as the initial velocity increases.

Prof. MINCHIN inquired whether the catenary could be best drawn by using a scale of equal parts instead of one divided reciprocally.

The PRESIDENT greatly appreciated the saving of labour effected by Mr. Boys' method, and thought the apparatus should be shown at the forthcoming Exhibition of Mathematical Instruments in Germany.

Prof. O. J. LODGE, F.R.S., read a paper on "*The Foundations of Dynamics*," in which he examines the objections raised by Dr. MacGregor (*Phil. Mag.*, Feb., 1893) against the views on "Newton's Laws of Motion and the Conservation of Energy," expressed by the author in 1885. The first part of the paper treats of the nature of axioms. An axiom or fundamental law is regarded as a simple statement suggested by familiar or easily ascertained facts, probable in itself, readily grasped, and not disproved, or apparently liable to disproof, throughout a long course of experience. On such bases the conservation of energy and of matter rest. Neither can be proved generally, but like other fundamental laws they fit into a coherent and self-consistent scheme, and are therefore worthy of acceptance until they are shown to be wrong.

The second part relates to the 1st and 3rd laws of motion. Dr. MacGregor objects to the 1st law on the ground that uniform motion is unintelligible unless its direction and velocity are specified with reference to a set of axes; and directly axes are introduced, difficulties occur as to their motion, because there is no satisfactory criterion of rest. Such notions the author deems artificial and unnecessary, except where it is required to define the absolute magnitude and direction of the motion. Reasoning from his own experiments he believed the ether was at rest, for he had not found it possible to move it by matter. The 1st law, he said, had been considered unnecessary as being only a particular case of the 2nd. While admitting the latter fact, he maintained that its separate statement was desirable, on account of its simplicity and its affording a practical definition of the mode of measuring time. As regards the 3rd law being deducible from the 1st, he pointed out that if it could be axiomatically asserted that the centre of mass of a rigid system moves uniformly unless an external force acts on the system, then the 3rd law follows. Newton apparently considered it best to state the 3rd law as an axiom, but to many persons it is not

obviously axiomatic (some engineers do not accept it), hence its deduction from the other two laws is useful.

Part III. of the paper deals with the deduction of the law of conservation of energy from Newton's 3rd law, and universal contact action. Dr. MacGregor objects to the author's definition of energy as the name given to "work done," and contends that this definition assumes conservation. On this point Dr. LODGE invited criticism, meanwhile pointing out that his definition was analogous to the customary definition of the potential function, and a name for the line integral of a force considered as a quantity that can be stored. On the basis taken, two bodies can only act on one another whilst in contact; hence, if they move they must move over equal distances. But their action consists of a pair of equal and opposite forces, therefore their activities are equal, and whatever one loses the other gains, *i.e.*, energy is transferred from one body to another without change in quantity. The law thus established, the author regards as more precise and definite than the ordinary law, because it implies not only the conservation but the identity of energy. The legitimate use of the phrase "potential energy" is discussed at some length, and the view that whenever energy is transferred it is also transformed, upheld.

In Part IV. the dissipation of energy, the nature of potential energy, and the 2nd law of thermodynamics, are considered. In discussing transference and transformation, "potential energy" is used to indicate the energy of a body under stress, and "kinetic energy," that due to sustained motion. Each corresponds to one of the factors of the product $F v$, "activity." So long as one factor is absent no activity can manifest itself; but directly the missing factor is supplied, transference and transformation begin. This was shown to hold in an example of an air-gun, with its muzzle plugged, chosen by Prof. MacGregor as an instance of transference of potential energy without transformation.

The law of dissipation of energy is stated thus:—"If a body has any portion of energy in such a condition that it is able automatically to leave the body, that portion usually does so sooner or later."

Instead of the ordinary form of the 2nd law of thermodynamics, the following statement is proposed:—"The portion of energy which a body can automatically part with is alone available for doing work."

In discussing this subject the author points out that the common notion that heat engines are much less efficient than water or electric engines is a mistake arising from the fact that in the one case the efficiency is calculated on the total energy, whilst in the latter cases only the available energy is considered.

Two appendices accompany the paper, one on the "Objectivity of Energy and the Question of Gravitation," and the other on "More detailed Discussion of the Transmission of Energy in Difficult Cases."

Prof. GREENHILL said the paper was full of suggestive ideas. He could not agree with all the views expressed in the paper on the subject of Newton's 3rd law. In considering action and reaction as equal and opposite, Newton ignored the inertia of the medium, and if this be included, the forces are no longer equal.

Mr. BOYS asked Prof. Greenhill if the first link of a chain pulled on the second link harder than the second pulled on the first?

Prof. S. P. THOMPSON thanked the author for getting rid of all square laws. He himself could not conceive of any effect being more than proportional to the cause.

Further discussion of the paper was postponed until next meeting.

Quantitative Determination of Cholesteroline.—J. Lewkowitsch (*Berichte*) recommends Benedikt and Ullzer's method for ascertaining the acetyl number or the determination of the iodine number according to Von Hübl.

NOTICES OF BOOKS.

Seventh Annual Report of Her Majesty's Inspectors of Explosives: being their Annual Report for the Year 1892. London: Her Majesty's Stationery Office.

It is most satisfactory to learn from this report that H.M. Inspectors of Explosives are still carrying out their duties successfully, and with an increased appreciation on the part of manufacturers, merchants, and the local authorities. It is here admitted that "there is no falling off in the high standard previously attained in the great majority of these establishments" (the manufactories of explosives), and that "the condition of the factories and magazines is now generally better than it was a year ago." It would even seem that more care and intelligence are now displayed by the workmen. This careless and obstinate neglect of precautions required by the law as well as by the factory regulations has been hitherto a danger not merely to the men themselves, but to all persons in the neighbourhood. Yet when a casualty has occurred a certain portion of the press has not scrupled to throw the blame upon the "cruel rapacity" of the masters who "compel" men to work under dangerous conditions!

Mischief occasionally still happens from miners having blasting powder in their houses and making up their own cartridges. Three miners in Northumberland have been convicted of this offence during the past year.

A welcome fact is that the quantity of gunpowder imported into Britain during 1892 has been smaller than in any year since 1879. On the other hand, our exports have reached a lower point than in any year since 1870.

Explosions of malicious origin have fortunately been rare in Britain. The worst case was that of the Walsall anarchists, convicted at Stafford Spring Assizes and sentenced to very inadequate terms of imprisonment.

We may here quote with approval an extract given from a pamphlet by Brigadier-General Henry Abbott, of the United States Army. He proposes that all persons guilty of outrages by means of explosives should, like pirates, be placed beyond the pale of the law, and should be at once hunted down in all civilised nations. "Recommendations to mercy" and verdicts of "extenuating circumstances" should, in their case, be prohibited.

After careful experiments, H.M. Inspectors have pronounced that arc lamps should in no case be used in a factory for explosives. Incandescent lamps should be protected by "at least one strong glass outer globe, so proportioned to the size of the lamp within that when the latter is burning under normal conditions the temperature of the outer globe shall not exceed 140° F."

No novel explosive of exceptionally remarkable properties has been introduced into manufacture in this country. No additional light has been thrown upon the nature of melinite, upon which our French neighbours rely for improving the Germans out of existence when the "war of revenge" breaks out. Had this compound been in course of manufacture by our authorities, every detail of its production would before this have become fully known to all our enemies, foreign or domestic.

Another source of public danger is too often ignored. Persons who may have been using "high" explosives sometimes carelessly leave cartridges, shells, &c., lying about. If such material falls into the hands of children or of criminals very serious results are probable. Of this not a few cases are here on record. Persons smoking whilst conveying ammunition imperil the lives of themselves and others.

A curious case seems to have occurred at New York:—"A labourer found a half-pound stick of frozen dynamite in a barrel of unslacked lime, just outside the pump-house, and proceeded to smash it with a brick. The engineer coming on the scene, and observing the nature of the material, speedily retired to a safe distance, from which

he directed the labourer what to do. Fortunately the dynamite did not explode; it was removed and taken out in a boat and dropped overboard. It is believed by the authorities that the dynamite was placed in the barrel by design." It was doubtless hoped that the moisture from the dynamite would slack the lime and cause an explosion!

The freezing of dynamite and the necessary thawing are abundant sources of accidents.

A very rare experience is that of a man who was blown to a distance of 120 feet by the explosion of a truck load of dynamite in consequence of a train leaving the metals. The man suffered no injury beyond a few bruises, though his clothes were entirely stripped off. The noise of this explosion, it is said, was heard to a distance of 35 miles.

Celluloid does not, in the opinion of H.M. Inspectors, come within the purview of the act, except made for use as an explosive. Moreover, it is not explosive, though certainly inflammable.

A doubtful case is recorded from Atherton, Lancashire. A man died, it is said, from inflammation of the brain resulting from the fumes given off on the explosion of a "roburite" cartridge. The case seemed chiefly to turn on the evidence of a local practitioner, who admitted that he had never heard of any similar case.

The list of authorised explosives is rather extensive. In many cases a chemist feels at a loss to account for the function of some of the ingredients.

The Inspectors certainly deserve great credit for the manner in which they are performing their duties.

Experiments upon Magnesia, Alba, Quicklime, and other Alkaline Substances. By JOSEPH BLACK, M.D., Professor of Chemistry in the University of Edinburgh, 1766—1797. Edinburgh: William F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co., Limited. 1893. Small 8vo., 47 pp.

THIS little work, the first of the "Alembic Club Reprints," has a very laudable object. It is intended to "enable students of chemistry to possess themselves of a copy of this most important contribution to the foundation of chemistry as an exact science," and secondly, "to place within the reach of every student of chemistry a model of clear reasoning and of inductive investigation, second in this respect to nothing which has appeared in much more recent times."

The facts disclosed by Dr. Black have of course been the common property of chemists for upwards of a century. But as a model for the "researcher" the book retains its full value, and may be studied with much advantage.

In Dr. Black's writings, as in those of some others of our earlier men of science, there is a sobriety, an indisposition to outrun demonstration, which may indeed serve as a lesson.

It is mentioned in the preface that the orthography and punctuation of Black's original paper have been retained, and there follows the welcome announcement that Mr. Clay will publish reprints of other important writings of our earlier chemists.

Detection of Phenols.—L. M. A. Lambert (*L'Union Pharmaceutique*).—The author applies the colour reaction obtained on dissolving iodoform in the phenol in question and adding potassa lye. Ordinary phenol, resorcin, phloroglucin, and pyrogallol give a rose and red colour, orcin and salicylic acid a reddish violet, guaiacal and thymol a violet, hydroquinone and the naphthols a blue. For iodoform, chloroform or bromoform may be substituted. The reaction may be used inversely for the detection of small quantities of iodoform, chloroform, chloral, or bromoform, especially in toxicological investigations. The colours obtained as above disappear on the addition of an acid, but reappear on adding excess of alkali.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 6.

Detection of Tubercle Bacilli in Sputum.—P. Kaufmann (*Centralb. f. Bakt. and Chem. Centralblatt*).—The preparation fixed on the cover-glass in the usual manner, but in a very thin stratum, is stained with hot carbolic magenta and then moved up and down for three minutes in water at 98—99°, so that only a faint rosy reflection is visible on the preparation. By this treatment most bacteria are decolourised, whilst the bacilli of tubercle and leprosy resist the decolourising at least for a considerably longer time. On microscopic examination the bacilli of tubercle appear dark red on a whitish grey ground.

Detection of Imitations of Amber.—Otto Helm (*Industrie Blätter and Pharm. Central-Halle*).—Genuine Baltic amber, when polished, displays in polarised light between crossed nicols faint interference colours, rarely such as are brilliant. Copal is softer than amber, more soluble and more fusible. Gedanite (brittle amber) is distinguished from true amber (succinite) by the absence of succinic acid. Celluloid may be detected by its odour of camphor.

Identity of Cystine and Ulexine.—A. Partheil (*Archiv der Pharm.*). Cystine, $C_{11}H_{14}N_2O$, forms large, colourless, anhydrous, prismatic crystals, not deliquescent. It melts at 152—153°, and can be sublimed *in vacuo*. It is soluble in water, alcohol, chloroform, and acetic ether; less readily in benzol, amylic alcohol, acetone, commercial ether, and hot ligroin. In cold ligroin it is almost insoluble and quite insoluble in petroleum ether, carbon disulphide, and pure ether. The solution of cystine turns the plane of polarisation to the left. Its most sensitive reagent is potassium bismuth iodide, with which it yields a brown precipitate. If cystine or one of its salts is covered with the solution of a ferric salt, there appears a blood-red colour, which disappears on dilution with water or on acidulation. If a few drops of solution of hydrogen peroxide are added to the blood-red liquid the colour disappears, but on gently heating on the water-bath is succeeded by a blue.

A Reagent for Aloes.—L. Schoutelen (*Oesterr. Ap. Vereines*).—A concentrated solution of borax produces in liquids containing aloes, on standing for 20 to 25 minutes, a green fluorescence, which disappears on long standing.

Determination of Acetone in Urine.—M. and A. Jolles (*Wien. Med. Wochenschrift*).—Acetone may be detected and estimated along with other volatile substances in the distillate with solution of phenylhydrazine. If acetone is present there is formed the corresponding phenylhydrazon, the quantity of which is determined according to H. Strache's process (*Monatshefte f. Chemie*).

Detection and Determination of Sugar in Urine.—E. Salkowski and M. Jastrowitz.—The authors have detected a new kind of sugar in the urine of a votary of morphine. With soda-lye and copper sulphate the urine gave a tardy but abundant precipitate of yellow cuprous oxide, but the fermentation test and polarisation gave negative results.

A New Reaction for Glucose.—O. Rosenbach.—On heating with alkali in a cold saturated solution of sodium nitroprusside, glucose and lactose give a deep brownish red or orange colour.

Determination of Colouring Matter in Blood.—F. Hoppe-Seyler (*Zeit. f. Physiol. Chemie*).—The author proposes a specially improved colorimetric process.

Detection of Biliary Constituents in Animal Fluids.—R. von Jaksch.—The author detects biliary pigments in the blood by allowing 10–15 cc. of the blood to coagulate, drawing off the serum with a syphon, filtering through a dense stratum of asbestos, and allowing it to congeal at 80° in a test-glass in the thinnest possible layer. Normal serum appears pale yellow and of a milky turbidity, whilst such as contains bile-pigment has a green colour.

Determination of Peptones and Albumoses in the Contents of the Stomach.—S. Riva-Rocei (*Centralblatt für Klin. Medicin*).—The author determines the total albumenoids by precipitation with absolute alcohol, drying and weighing; the coagulable albumenoids by Devoto's method, and the sum of the coagulable albumenoids and albumoses by saturating the liquid (previously acidulated, if necessary, with acetic acid) with magnesium sulphate, washing the precipitate with a solution of the same salt, drying at 110°, weighing, and incinerating. From the weight of the last precipitate he deducts the ash, with an addition of 15 per cent.

Gutzeit's Arsenic Test.—Curtmann (*Chem. Zeit.*).—There is danger that coal-gas present in the space examined may occasion a reaction, and that not every kind of paper is fit for use. Nagelfort (same journal) avoids this danger by causing the hydrogen to act upon finely pulverised silver nitrate placed between glass-wool in a U-tube. The slightest yellow arsenic reaction can easily be detected among the snow-white glass-wool.

Elimination of Poisons in the Soil.—F. Falk and R. Otto (*Vierteljahr. für Gerichtl. Medicin und Sanitätswesen*) found that upon pouring solutions of alkaloids (1 per cent and 10 per cent solutions of strychnin and nicotin) upon soils, whether sandy or humic, there ensued a certain absorption of the poison or its transformation into harmless products. This action was decidedly stronger in humic soils, and feebler in sandy soils, but it was observed even in sterilised samples of soils, so that the decomposition of the alkaloids cannot be ascribed to the micro-organisms of the soil. The eliminating power of the soil is limited, and as soon as it is exhausted the alkaloidal solution passes through unchanged. Pure cultures of tetanus were rendered inert by passage through humus, but it is merely enfeebled by sand. In forensic chemistry the disappearance of alkaloids on filtering their solutions through soil is especially important.

Fungus Poisons.—Kobert (*Dorpat Naturf. Gesell.*, 1891).—No chemical details are given.

New Reaction for Cocaine.—Aloys Kuborne, jun. (*Pharm. Central Halle*).—A little cocaine is laid in a small porcelain capsule and covered with about 1 c.c. nitric acid of specific gravity 1.4, evaporated to dryness on the water-bath, cooled, and to the cold residue there is added a drop of alcoholic solution of potassa. No colour appears (distinction from atropin), but if the capsule is replaced on the water-bath there suddenly appears an intense violet colour.

Poisonings with Strychnin and Brucin.—Collin (*Pharm. Zeitung*) gives microscopic distinctions between the powders of the two seeds.

New Determination of the Atomic Weight of Cadmium.—H. N. Morse and H. C. Jones (*American Chemical Journal*).—The authors arrive at the value 112.0706 (O = 16).

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This number contains no original matter.

MEETINGS FOR THE WEEK.

- TUESDAY, 30th.—Royal Institution, 3. "The Waterloo Campaign," by E. L. S. Horsburgh, M.A.
— Society of Arts, 8. "American Silver Work," by Horace Townsend.
— Institute of Civil Engineers, 8. (Anniversary).
- THURSDAY, June 1st.—Royal, 4.30.
— Royal Institution, 3. "The Geographical Distribution of Birds," by R. Bowdler Sharpe LL.D.
— Chemical, 8. "Azo-compounds of the Ortho Series," by Prof. Meldola, F.R.S., and B. Burls. "The Fluorescence of Camphoric Anhydride," by Dr. Collie. "The Action of Phosphoric Chloride on Camphene," by J. E. Marsh, M.A., and J. A. Gardner, M.A. "The Composition of Jute produced in England," by A. Pears, jun.
- FRIDAY, 2nd.—Royal Institution, 9. "Study of Fluid Motion by means of Coloured Bands," by Prof. Osborne Reynolds, F.R.S.
— Geologists' Association, 8.
— Quekett Club, 8.
- SATURDAY, 3rd.—Royal Institution, 3. "Falstaff": a Lyric Comedy by Boito and Verdi, by Dr. A. C. Mackenzie.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1749.

ON THE ABSORPTION-SPECTRA OF SOME COMPOUNDS OF CHROMIUM.*

By W. LAPRAIK, Ph.D., F.R.C.

(Concluded from p. 246).

Absorption-Spectrum of a Solution of the so called Perchromic Acid (32).

It was thought to be of some interest to examine other compounds of chromium of a totally different constitution to the foregoing, in order to see how far their absorption-spectra differed from the previous compounds examined. With this idea in view, a solution of the fine blue coloured compound—the so-called perchromic acid—was prepared by the addition of hydrogen peroxide to a solution of chromic acid. I found the compound so unstable that I had great difficulty in making an observation; especially was this the case in solutions of such a degree of concentration as to give an absorption-spectrum in such thicknesses as 3 to 4 c.m. But by using a much more dilute solution, and increasing the thickness to about 10 c.m., I was able to measure the bands with the following result:—Continuous absorption to 740. Then two definite bands at 689–674 and 653–639 respectively. The broad absorption at 613–544 and continuous absorption from 448 (32).

In a thicker layer or a more concentrated solution, the two bands in the red join on to the absorption on either side, so that there is a narrow band of red light transmitted from 674 to 653; also the absorption in the green becomes somewhat broader while the blue light is transmitted.

This blue compound is known to be soluble in ether, but I found this solution so unstable that I was unable to make any measurements, but its absorption-spectrum appeared to be like the aqueous solution.

Some Salts of the Chrom-Ammonium Bases.

I was fortunate in having placed at my disposal for the purpose of this research some specimens of salts of the chrom-ammonium bases. It was thought that it would be of considerable interest to spectroscopically examine these bodies, which differed so widely in chemical constitution from the compounds of chromium previously examined.

These salts have been the subject of several investigations by Jørgensen (*Fourn. Prak. Chemie*, [2], 20, 105; [2], 25, 321; [2], 42, 206; [2], 44, 63).

Solutions of the salts were made in subdued light, and they were examined without loss of time, as it is known that light decomposes many of them.

Chloro-Purpureo-Chromium Chloride (33 and 34), $\text{Cl}_2[\text{Cr}_2\text{IO}(\text{NH}_3)]\text{Cl}_4$.

This salt was first examined, a cold aqueous solution was made, and a layer 10 c.m. thick was used. This gave a continuous absorption to 695. Then a narrow band at 674, which has sharp edges, but it is not very dark; and then continuous absorption from 585 (33). By taking a thinner layer of solution—2 c.m. thick—the latter absorption was broken up. It began as a slight shadow at 545, and gradually reached a maximum at 474, where it stopped. But in the thinner layer the band 674 was no longer visible, and the continuous absorption was from 415 (34).

Xantho-Chromium Chloride (35 and 36), $(\text{NO}_2)_2[\text{Cr}_2\text{IO}(\text{NH}_3)]\text{Cl}_4$.

An aqueous solution of this salt was made, and a layer of 15 c.m. thickness examined (35). It gave continuous absorption to 698. Then a narrow sharp band at 674, and then continuous absorption beginning with a shadow at 585, but dark at 572.

A thinner layer—2½ c.m.—splits up the latter absorption, which begins as a shadow at 544, then gradually reaches a maximum, and ending at 444, and the blue light which is transmitted is somewhat obscured. These effects are no doubt due to the presence of the NO_2 group in the salt. The narrow band 674 was again absent in the thinner layer, and the continuous absorption began at 414.

Rhodo-Chromium Chloride (37 and 38), $(\text{OH})[\text{Cr}_2\text{IO}(\text{NH}_3)]\text{Cl}_5 + \text{H}_2\text{O}$.

An aqueous solution of this salt was made; it had a fine rose colour, and a layer of the solution of 15 c.m. thickness was examined, which gave continuous absorption to 740, with a shadow to 704; then a narrow, sharp, but not a dark band at 674; then two sharp lines, which are very close together, so that they are apt to be mistaken for a single band at 663 and 660 respectively; then a slightly thicker band, but not so dark and less distinct than the others at 650, and continuous absorption from 599. (37).

A thinner layer—2½ c.m. thick—gave continuous absorption to 800, with a shadow to 704. The four bands previously mentioned were not visible in this thickness, but the broad absorption was seen from 546 to 473, and continuous absorption from 413.

Leuto-Chromium Nitrate (39), $[\text{Cr}_2\text{I}_2\text{NH}_3](\text{NO}_3)_6$.

An aqueous solution of this salt having a thickness of 15 c.m. was examined. Its absorption-spectrum is quite different from the previous salts, and is as follows:—Continuous absorption to 701, which joins the first band at 683. Then follow three other bands, narrow and sharp, at 660, 650, and 631 respectively, the last being rather broader than the others; then a shadow at 599, which joins the continuous absorption at 536. (39).

In a thinner layer—2½ c.m.—of solution, all these bands fade out, and there is only continuous absorption from 510.

Chloro-Purpureo-Cobalt Chloride (41).

A solution of this salt—15 c.m. in thickness—did not give any absorption bands, but only continuous absorption; but a layer of solution of 2½ c.m. thickness gave continuous absorption to 710, a broad absorption from 571 to 467, and continuous absorption from 414. This salt does not behave, therefore, like the salts of the chrom-ammonium bases, as it does not give absorption bands in the red part of the spectrum with the thickness of solution used.

It thus seems that the following compounds—chloro-purpureo-chromium chloride, xantho-chromium chloride, and rhodo-chromium chloride—all give the band 674 in layers of greatest thickness of solution. These salts all contain the radicle $[\text{Cr}_2\text{IO}(\text{NH}_3)]$, and it would therefore appear that this band is due to this radicle, for the compound leuto-chromium nitrate does not contain it, but the radicle $[\text{Cr}_2\text{I}_2\text{NH}_3]$, and does not give the band referred to. Further, the bands 660 and 650 which occur in leuto-chromium nitrate appear also in exactly the same position in rhodo-chromium chloride. It is not quite evident from the usually accepted formulæ for these bodies why this should be the case, but it would appear that they have some part of their molecule of the same structure.

Some Double Cyanides of Chromium and Cobalt.

Potassium Chromi-Cyanide, $\text{K}_6\text{Cr}_2(\text{CN})_{12}$ (40).—An aqueous solution of this salt had a yellow colour in a layer of 15 c.m. thickness. It gave for the chromium

* *Fourn. für Prakt. Chemie*, xlvii., 305 (1893).

	Continuous absorption.	1.	2.	3.	4.	5.	Continuous absorption.
1. Potassium chromoxalate, crystallised	800	717	710—704	683	663	660—518	434
2. Potassium chromoxalate, saturated solution	820	710	704—698	681	663	642—508	474
3. Chromium oxalate solution	714	—	704—689	—	653	610—503	471
4. Chromium oxalate solution with an excess of oxalic acid	800	710	704 695	681	663	650—505	471
5. Red potassium chromoxalate solution	800	710	704 695	681	663	633—502	467
6. Ammonium ferric oxalate solution ..	698. 623	—	—	—	—	—	489
7. Potassium manganic oxalate solution	704	—	—	—	—	—	601
8. „ cobaltic „ „	770. 710	—	—	—	—	657—543	469
9. „ cupric „ „	639	—	—	—	—	—	411
10. „ chrom-malonate „	—	714	701	681	660	655—507	465

Chromium hydroxide dissolved in aqueous solutions of the following acids:—

11. Malonic acid	714	—	695—689	—	—	655. 623—503	464
12. Succinic „	740	727—715	707	693	679—670	655. 644—537	498
13. Formic „	800	721—714	704	689	674—666	650. 611—544	470
13a. Acetic „	800	721—714	704	689	676—668	648—549	483
14. Propionic acid	800	729—717	707	689	676—668	655. 641—544	494
15. Butyric „	800	729—717	707	689	676—668	644—544	480
15a. Isobutyric „	800	729—717	707	689	676—668	644—544	482
15b. Valerianic „	800	730—718	707	692	677—669	650—517	484
16. Heptylic „	800	732—719	708	695	681—674	650—544	480
17. Monochloracetic acid	740. 710	—	698—686	—	—	655—504	480
18. Dichloracetic „	740. 721	—	689—681	—	—	655—513	480
19. Trichloracetic „	740. 714	—	701—674	—	—	655—509	480
20. Tribromacetic „	770	—	—	—	676—668	653. 610—534	459
21. Glycollic „	758	723—714	706—695	—	—	670. 644—507	473
22. Lactic „	770	721	707	—	676—665	629—533	467
23. Trichlorolactic „	721	—	710	—	674	655. 610—526	483
24. Phosphoric „	740	—	698—686	—	670—650	639. 621	471
25. Malic „	729	—	707—695	—	—	670. 644—498	480
26. Tartaric „	800	—	707—695	—	—	668. 639. 501	475
27. Citric „	736	—	707—698	—	—	660. 629. 504	467
28. Isethionic „	717	—	695—668	—	—	653—506	480
29. Chromium chloride solution	717	—	704—689	—	—	653. 619—550	472
30. Colloidal chromium chloride solution	800—750	—	710—695	—	—	665. 621—544	480
31. Chromium hydroxide	721	—	710—692	—	—	665—617—547	473
32. Perchromic acid	740	—	—	689—674	653—639	613—544	448
33. Chloro-purpureo-chromium chloride, 10 c.m. thick	695	—	—	674	—	—	585
34. Chloro-purpureo-chromium chloride, 2 c.m. thick	717	—	—	—	—	545—474	415
35. Xantho-chromium chloride, 15 c.m. thick	698	—	—	674	—	—	585—572
36. Xantho-chromium chloride, 2½ c.m. thick	698	—	—	—	—	544—444	414
37. Rhodo-chromium chloride, 15 c.m. thick	740—704	—	—	674 663 660 650	—	—	599
38. Rhodo-chromium chloride, 2½ c.m. thick	800—704	—	—	—	—	546—473	413
39. Leuto-chromium nitrate 15 c.m. thick	701	—	683	660	650 631	—	599—536
40. Potassium chromi-cyanide, 15 c.m. thick	710	—	545—542	531—525	520—518	507—505	476
41. Chloro-purpureo-cobalt chloride ..	710	—	—	—	—	571—467	414

compounds an unique absorption-spectrum (40). Continuous absorption to 710; then four bands at 545—542, 531—525, 520—518, and 507—505 respectively, and continuous absorption from 476.

I am not acquainted with any other compound of chromium giving absorption bands analogous to these, and further, this salt does not give the broad absorption in the green part of the spectrum so typical of most other compounds of chromium.

Potassium Cobalti-Cyanide, $K_6Co_2(CN)_{12}$.—A concentrated aqueous solution of this salt was used. It gave no absorption bands, nor did it give the broad absorption in the green and blue part of the spectrum which is known to be so typical of the cobalt salts.

Conclusions.

1. The absorption-spectra of the salts examined, having the general formula $M_6Cr_26C_2O_4$, is the same when compared in solution, and also when compared in the solid state; but the absorption-spectrum in the solid state differs from the absorption-spectrum of the same salt in solution, the bands in the former case being nearer the less refrangible end.

2. Chromium oxalate has been obtained, analysed, and its absorption-spectrum recorded, which has been shown to differ from that given by the complex salts.

3. It has been shown that a solution of chromium oxalate with an excess of oxalic acid yields (a) the same absorption-spectrum as a solution of Croft's salt,—

$K_2Cr_2O_4 \cdot 4C_2O_4$,—(b) while with a larger amount of oxalic acid it yields an absorption-spectrum identical with that given by the salts $M_6Cr_2O_4 \cdot 6C_2O_4$, and the conclusion has been drawn that analogous hydrogen compounds exist in solution.

4. The corresponding complex oxalates of iron, manganese, and cobalt do not yield analogous absorption-spectra.

5. A salt of malonic acid, analogous in composition to the corresponding oxalic acid compound, has been obtained. It has been analysed, and its composition is $K_6Cr_2O_4 \cdot 6C_3H_2O_4 + 6H_2O$. Its properties and absorption-spectrum are given.

6. The absorption-spectra given by the solution of chromium hydroxide in the various organic acids used have been noted and compared, and their relations to chromium hydroxide have been shown.

7. The absorption-spectra given by solution of chromium hydroxide in the fatty acids are similar in character, but the absorption bands are moved towards the less refrangible end in the case of the higher acids of the series.

8. The band 710—692 is represented in all the compounds of chromium examined,—except in potassium chromi-cyanide,—sometimes moved to the less, sometimes to the more refrangible end of the spectrum.

9. The broad absorption in the green—650 to 550 approximately—is represented in all the compounds of chromium. Sometimes it is moved towards the red end of the spectrum, as in the case of chromium hydroxide, dissolved in an excess of phosphoric acid; sometimes it is moved towards the blue end, as in the case of the salts of the chrom-ammonium bases; and in the case of potassium chromi-cyanide it appears as a series of bands.

10. It has been shown that the salts containing the group $[Cr_2IO_4NH_3]$ give an absorption band at 674.

In conclusion, my best thanks are due to Professor E. Wiedemann for the kind help he has given me, and also for placing at my disposal his specimens of the chrom-ammonium and other analogous salts.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

FIRST PAPER: THE ANALYSIS OF BARIC BROMIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 247).

The Properties of Baric Bromide.

BARIC bromide crystallises from aqueous or dilute alcoholic solutions in doubly terminated monoclinic prisms, which are somewhat hygroscopic, but not deliquescent in ordinary weather.

The crystallised salt contains two molecules of water, together with the slight excess which is usually to be found in such crystals. Below the temperature of 70° in somewhat moist air, or at the ordinary temperature in perfectly dry air, it loses one of these molecules.† The other one is retained until a temperature of from 100° to 130° is reached, according to the hygroscopic condition of the surrounding air.

The accuracy of the final result for the atomic weight of course depends upon the complete absence of water from the dried salt; hence an especial series of experiments was made to determine the conditions under which

the water was completely expelled. Upon heating to redness, the salt is very slightly decomposed (Schultze, *Journ. Prakt. Chemie*, [2], xxxi., 407); hence in all cases where a high heat was used, the amount of baric hydroxide and baric carbonate formed were determined by means of very dilute standard hydrobromic acid, using phenolphthalein and methyl orange respectively as the indicators. The accuracy which it is possible to attain in this process was a great surprise. If a very small amount of pure boiled water is used for the solution of the baric bromide, a deficiency of less than a tenth of a m.grm. of bromine in 5 grms. of the salt is detected with the greatest ease. The correction applied to the weight of the baric bromide was of course always the calculated difference between the weights of the bromide and the hydroxyl, or the carbonic acid, which had taken its place. For example, a deficiency of 0.81 m.grm. of hydrobromic acid, found by alkalimetry, involved a correction of 0.63 m.grm. if the alkaline earth had been found in the form of hydroxide, or 0.50 m.grm. if it had been found in the form of carbonate. Since baric carbonate is very faintly alkaline to phenolphthalein, this correction is not absolutely exact; but its error is an infinitesimal one so far as this work is concerned. It is probable that, if any traces of oxide were formed, they were converted into hydroxide or carbonate before the crucible cooled.

One experiment showed that 1.6 grms. of baric bromide dried at 136° lost 0.4 m.grm. on being heated to dull redness. On another occasion, 3 grms. of baric bromide which had been dried at 200° to constant weight lost 0.50 m.grm. upon heating to dull redness. Alkalimetry indicated that 0.32 m.grm. should be added to the last weight as a correction for the bromine lost; hence the corrected loss was 0.00018 grm., or 0.006 per cent. A third trial gave the corrected loss of 3.5 grms. of baric bromide between 185°, and a dull red heat as 0.00027 grm., or 0.008 per cent. Again, 3.4 grms. of a less pure specimen of the salt lost 1.2 m.grm. between 200° and dull redness, of which loss eight-tenths of a m.grm. was accounted for by the baric carbonate found in the dissolved residue. In Experiment 19 about 3.5 grms. of the salt dried at 260° lost 0.04 m.grm. on heating to 340°, and 0.27 m.grm. more upon subjection to a red heat. In order to prove that the method of desiccation over sulphuric acid was sufficient for the purpose in hand, this specimen was again heated to 400°, and cooled in a vacuum over phosphoric oxide. After the admission of dry air the crucible and contents were found to have gained a little less than a twentieth of a m.grm. Since seventeen one-hundredths of a m.grm. must be added to the last weight of the salt to correct for the amount of alkali found, it is evident that the salt dried at 340° in the first place could not have retained more than 0.005 per cent of water, which could be expelled at a red heat.

The most severe test of the hygroscopic constancy of baric bromide was obtained by fusion. 17.4841 grms. of baric bromide, which had been thoroughly dried at a dull red heat, were fused in a platinum crucible, and were found to have lost 4.1 m.grms. during the process. 2.25 c.c. of twentieth normal hydrobromic acid were required to render the solution of the clear cake neutral to phenolphthalein, and 0.10 c.c. more made it strongly acid to methyl orange. These figures involve a correction of 7.0 m.grms. to the second weight of baric bromide, making it 17.4870 grms. The excess of this weight over the first (17.4841) is completely accounted for by the knowledge that a slight indeterminable correction (from 0.010 to 0.03 per cent) should have been applied to the earlier one, owing to its previous loss of bromine. The crucible was found to have lost 0.20 m.grm.

Again, 2½ grms. of baric bromide heated to constant weight at 185° lost 2.11 m.grms. on being fused in a double crucible. Of this weight all but 0.17 m.grm. (0.007 per cent) was accounted for by the amount of alkali found in the dissolved residue (Experiment 13). In

* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

† Werther (*Journ. Prakt. Chemie*, xci, 167); also Von Hauer (*Journ. Prakt. Chemie*, lxxx., 230). Rammelsberg states that the salt is isomorphous with baric chloride (*Pogg. Ann.*, lv., 237).

‡ 2.8688 grms. of crystallised baric bromide lost 0.1547 grm. on heating to constant weight at 70°—80°; the residue lost 0.1533 grm. more upon heating to constant weight at 160°. Compare Graham Otto ("Michaelis," iii., 662). 2.0506 grms. of baric bromide, which had been powdered and dried over sulphuric acid to constant weight, lost 0.1181 grm. upon drying at 200°.

Experiment 4, given below, the bromide was also fused. Although this sample was not weighed at any lower temperature, it is evident from the amount of silver it required that about the same relation must hold true. It is a necessary conclusion from these results that baric bromide loses no more water upon fusion than upon being heated to dull redness without fusion. This constancy of hygroscopic condition gives strong ground for the inference that the ignited salt is wholly free from water, and that the salt dried at 180° contains only about seven-thousandths of one per cent of the impurity. Moreover, it is very unlikely that water and baric bromide could remain together at a red heat without mutual decomposition. The question of the absolutely anhydrous condition of most substances must necessarily be a matter of inference, because our methods for the determination of a few tenths of a m.grm. of water in the presence of a large amount of other material, which may be volatilised, are not sufficiently accurate to furnish direct evidence upon this point. Our knowledge regarding baric bromide is hence as full as it is possible to obtain.

The specific gravity of baric bromide has been determined by Schiff (*Liebig's Annalen*, cvii., 59; also cviii., 23). According to his results the crystallised salt is 3.69 times heavier than the same volume of water, while the anhydrous salt is 4.23 times heavier. Since it is important in reducing weights to the vacuum standard to know the exact values of these physical constants, new determinations were made. Carefully re-distilled dry toluol, in which baric bromide is insoluble, was taken as the liquid to be displaced, and two specific gravity bottles were used. The weight of water filling the first bottle was found upon three trials to be 11.4117, 11.4133, and 11.4120 grms., these values being corrected to 4° for the expansion of the water, but not corrected for the expansion of the glass (24°) nor for the air displaced by the water and weights. An approximate determination of the coefficient of expansion of toluol gave the means of reducing all the weighings with that liquid to the same standard of 24° . Three weighings gave results for the weight of toluol, filling the bottle, to be 9.8357, 9.8356, and 9.8342 grms.; and 4.4262 grms. of large clear crystals of baric bromide were found to displace 1.0141 and 1.0126 grms. of toluol at 24° . Hence the specific gravity of crystallised baric bromide at 24° , compared with water at 4° , is 3.852. No correction is made for the difference in volume of the weights employed.

A sample of baric bromide was dried at 200° , powdered very rapidly, transferred to the specific gravity bottle, and heated for a long time at the softening point of glass. After cooling in a desiccator, the weight of the baric salt was found to be 7.6808 grms. After filling with dry toluol, removing the atmospheric pressure, and shaking as usual, the gain in weight was 8.3878 grms., as a mean of two closely agreeing trials. Since the volume of the pycnometer had slightly altered during the heating, the bottle was remeasured and found to contain 11.3338 grms. of water at 4° (not corrected for the expansion of the glass), and 9.7685 grms. of toluol at 24° . These data give a result for the specific gravity of anhydrous baric bromide equal to 4.794.

Since the apparatus was not perfect, a new specific gravity bottle was prepared, which gave far more concordant results. With this apparatus 5.7271 grms. of baric bromide, dried for a long time at 200° , were found to displace the same volume as 1.1979 grm. of water at 4° . Here again the salt and toluol were at 24° , and the weights were not corrected for the different volumes of the brass. These figures indicate a specific gravity of 4.781,—not very different from the previous result, but very different from the value obtained by Schiff. The value 4.79 is used in all calculations which follow.

One hundred parts of water dissolve about 100 parts of anhydrous baric bromide at ordinary temperatures, and nearly 150 parts at the boiling-point of water.* The salt

was found to be much less soluble in alcohol than one would expect from the literature on the subject.

A saturated solution in 87 per cent alcohol contains only about 6 per cent of baric bromide at the ordinary temperature. In absolute alcohol the salt is even less soluble. These facts had an important bearing on the methods of purification.

(To be continued.)

RESEARCHES ON SAMARIUM.

By LECOQ DE BOISBAUDRAN.

BOTH absolutely and with relation to the orange of Sm the band $Z\zeta$ is strengthened if we take the reversed spark not at the edge but in the middle of the liquid. The quantity and the nature of the acid also modify the relative brightness of the two bands.

For the experiments summarised below I have employed samaria, tolerably pure, but not fractionated.

Action of HCl.—The aqueous solution of samarium chloride, approximately neutral, shows on reversal the band $Z\zeta$, very faint, and much inferior to the orange. On adding HCl to the liquid, the $Z\zeta$ is decidedly increased, and under favourable conditions it may even become as strong as the orange.

It is essential to have very clear solutions, and to use an earth which has been carefully cleansed, as the least impurities seem very injurious to the formation of $Z\zeta$.

Action of NH_4OH .—With an aqueous solution of samarium nitrate, almost neutral, the band $Z\zeta$ is ordinarily much fainter than the orange. But if we add to the liquid a sufficiency of nitric acid, $Z\zeta$ becomes very decidedly stronger than the orange, at least in concentrated solutions. Without reaching such an intensity $Z\zeta$ is strengthened if we add nitric acid to a hydrochloric solution of Sm.

The band $Z\zeta$ has not the same aspect with HCl and with NH_4OH . In HCl it is well defined on the right, but very vague towards the red. In NH_4OH the right margin is rather cloudy, and the left margin is merely a little more so than the right. The place of the right edge of the band with HCl is obscure with NH_4OH , but the centre seems to be very little displaced. The dis-symmetry of the band in HCl renders the measurement of the centre difficult.

Approximate Positions observed with Spectra of Mean Intensity.

$Z\zeta$ in HCl, apparent middle	$\lambda = 614.4^*$
" " right margin	$\lambda = 611.8^{\dagger}$
$Z\zeta$ in NH_4OH , apparent middle	$\lambda = 615.5$
" " right margin	$\lambda = 614.4$

Action of Acetic Acid.—With an aqueous solution of neutral samarium acetate $Z\zeta$ was not visible. On adding to the liquid from one-half to three-quarters of its volume of acetic acid, the fluorescence is slightly increased, but $Z\zeta$ did not appear. The addition of a noteworthy quantity of nitric acid caused $Z\zeta$ to appear, but it was still much fainter than the orange. On a large addition of nitric acid $Z\zeta$, however, becomes almost equal to the orange.

Samaria was dissolved in nitric acid in excess, and the solution was divided into two equal parts.

A certain volume of water having been added to A, the band $Z\zeta$ appeared very visible, though fainter than the orange.

A volume of acetic acid (8° , and sold as pure) equal to one-half the volume of the water put into A, was added to B. $Z\zeta$ was then visible, but much fainter than with A. There was then added as much acetic acid as had

* The intensity being greater to the right than the left, the real centre must lie a little more to the left.

† The position of the right margin is too much to the left.

* See Graham Otto, *loc. cit.* Also recent experiments here.

been already introduced (in all the same quantity as the water put to A), Z ζ was weakened and became much fainter than it had been with A.

The acetic acid (or the impurities which it contains), appears therefore to prevent the production of the band Z ζ .

Comparison of Z β and Z ζ .—I have mentioned the increase of these fluorescences, obtained by taking the spark from the middle of the liquid, and their decrease in presence of ferric chloride. Z α and Sm are, on the contrary, more or less enfeebled if the spark springs at the middle of the liquid, and are less sensitive to the action of ferric chloride.

In presence of an excess of HCl Z β and Z ζ behave in an analogous manner, and are increased, especially Z β , whilst Z α is so to a less degree.

Nitric acid, on the contrary, causes Z β and Z ζ to undergo very different variations, Z ζ being much augmented and Z β much less.

Comparison of Z α and Z β .—An earth rich in Z α and Z β was dissolved in HCl. It was evaporated to dryness and taken up in water. In this aqueous solution Z α was much stronger than Z β . On adding to the liquid half its volume of nitric acid Z α and Z β were increased, Z α still remaining stronger than Z β . As much HCl was then added as there had been nitric acid previously introduced, Z α decreased a little (dilution of the solution?), but Z β was much strengthened, and surpassed Z α .

A larger proportion of earth in the hydrochloric and nitric solutions seemed to favour Z β compared with the orange of samarium.

We learn from the foregoing that the comparison of the reversal bands, Z ζ and orange, is somewhat delicate to effect in the various numbers of a fractionation.—*Comptes Rendus*, cxvi., p. 674.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 29TH, 1893.

By WILLIAM CROOKES, F.R.S.,

and

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act*, 1871.

London, May 15th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

By reason of the prevailing drought, the condition of the rivers throughout the month of April was exceptionally good, and the river-derived water supply was accordingly noticeable for the exceeding smallness of the proportion of organic matter present therein. Thus, calculated upon the amount of organic carbon found, the mean proportions of organic matter present in the different

supplies may be taken as being approximately about one-tenth part of a grain per gallon in the case of the New River Company's water, and about one-seventh part of a grain per gallon in the case alike of the Lea-derived water furnished by the East London Company, and of the Thames-derived water furnished by the other five companies. As a result, moreover, of the excellent condition of the streams themselves, the difference in quality of the water supplied during the month, by the companies having a large, and by those having but a small storage area, was inappreciable. The degree of freedom from colour tint of the water, expressed in the case of the Thames-derived supply by the blue-brown ratio 20 : 11.5, as a mean, was, although high, not so high as has been noticed on other occasions of an exceptionally low reduction of the proportion of organic matter present in the water.

It is interesting to compare the results afforded by the water supply for April with those afforded by the supply for February, which was an exceptionally wet month, and with the average of those afforded by the supply for the first three months of the year, including of course February, as exhibited in the following abstract of results obtained with the Thames-derived supplies:—

1893.	Oxygen required for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Maxima.
February	0.069	0.201	0.269
First three months ..	0.059	0.177	0.272
April.. .. .	0.028	0.088	0.125

It will be noticed that during February, when the river was in a flooded state and the water supply in a less satisfactory condition than usual, the absolute excess of organic matter present in the supply for that month above the exceptionally small amount present in the supply for April was really very small, amounting in the case of the Thames-derived supplies taken for illustration, to not more than one-fifth part of a grain per gallon, that is, to less than the three-thousandth part of 1 per cent. It is further noticeable that while the mean ratio of nitrogen to carbon in the organic matter of the April supply was found to be as 29 : 100, the mean ratio in the organic matter of the February supply was only as 21.5 : 100, indicating the mainly vegetable origin of the excess of organic matter then present—and, indeed, it seems to be an invariable rule that when the quantity of organic matter present in the water is somewhat above the average, its mainly vegetable character is proportionally more decided.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.

THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Continued from p. 248).

Copper.

THE estimation of this metal is effected by precipitation as copper sulphide (CuS) by means of sulphuretted hydrogen or hyposulphate of soda, with subsequent conversion into copper oxide (CuO), either by ignition or dissolving and re-precipitating with caustic soda (NaHO). Ten grms. of the iron or steel are digested for a considerable time at a gentle heat, with 100 c.c. of nitro-hydrochloric acid, and the solution eventually carried down to dryness. To dissolve the dry residue add a small quan-

* From *Industries*, April 4, 1893.

tity of hydrochloric acid, heat gently, and again take to dryness. Finally, re-moisten with a little hydrochloric acid, heat until solution is effected, dilute with hot water, and separate the silicon, &c., by filtration. The whole of the copper is contained in the filtrate, but before proceeding with the precipitation it is advisable to reduce the iron from the ferric, in which form it exists, to the ferrous state. This is accomplished by adding to the filtrate, made with water to a volume 250 c.c., an excess of sodium sulphite, and boiling until the sulphurous acid is expelled. To ascertain whether reduction is complete, a drop of the liquid is withdrawn at the end of a glass rod and brought in contact with a weak solution of sulphocyanide of potassium, when no red colouration should be found. The reduction of the iron is not absolutely necessary, as the same is effected by the sulphuretted hydrogen subsequently used for the precipitation of the copper, but by employing the sulphite the quantity of the sulphuretted hydrogen required is considerably lessened. Through the reduced solution pass a current of sulphuretted hydrogen until it is present in excess, allow to stand until the precipitated black copper sulphide (CuS) has completely settled, and pass the supernatant liquid through a Swedish filter-paper. Throw on the precipitate with the last portions, wash with water containing a little sulphuretted hydrogen, pierce the filter-paper, rinse the copper sulphide by means of a dilute solution of nitric acid into a beaker, some strong nitric acid being added, and the beaker and contents gently heated. When the whole, with perhaps the exception of a little free sulphur, has dissolved, the solution is diluted and filtered. The filtrate is then heated to boiling, a solution of caustic soda (NaHO) added, and the boiling continued. This results in the precipitation of the copper as copper oxide (CuO), which is collected on a filter, washed until free from alkali, ignited, contained in a porcelain crucible, and weighed. A hundred parts of copper oxide contains 79.85 parts of metallic copper.

A far more expeditious and less tedious method consists in precipitating the copper as CuS by means of sodium hyposulphite, with subsequent conversion of the sulphide into oxide by ignition. The details of the method are as follows:—

In a beaker place 10 grms. of the sample, cover with 100 c.c. of dilute sulphuric acid (one part acid to three of water), and digest at a gentle heat. To the resulting solution add 6 c.c. of a strong solution of hyposulphite of soda, bring to boiling, with constant stirring, maintain at this temperature for twenty to thirty minutes, during which time the copper will be precipitated as black copper sulphide (CuS), and the solution, which, upon the addition of the "hypo" became milky, has regained its green colour. Collect the precipitate as rapidly as possible on a filter, wash a few times with water, pierce the bottom of the filter-paper, and rinse the contents into the vessel in which precipitation took place. Dissolve the copper sulphide in nitro hydrochloric, and evaporate the resulting solution, after the addition of about 10 c.c. of strong sulphuric acid, until heavy white fumes commence to appear; when diluted with water, heat to boiling, and add an excess of ammonia. Allow to stand in a warm place until any precipitate formed has completely settled; subsequently pass through a Swedish filter-paper, which, together with its contents, are well washed with water containing a little ammonia. Expel the excess of ammonia from the filtrate by boiling, and re-precipitate the copper as CuS, as before, by the addition of a little hyposulphide of soda solution. Filter, wash, ignite, and weigh the resulting copper oxide (CuO).

For the determination of very minute quantities of copper, dissolve 20 to 50 grms. of the metal in nitro-hydrochloric acid, evaporate nearly to dryness, digest the residue with an excess of ammonia, and compare the colour of a measured quantity of this ammonia solution with that of a standard solution of copper coloured with

ammonia, or precipitate the Cu by any of the methods given.

Tungsten.

The method of detecting and determining tungsten is comparatively easy, as upon treating the iron or steel containing the metal with nitrohydrochloric acid, with subsequent evaporation to dryness and resolution, the tungsten is converted into tungsten anhydride (WO_3), and the silica is coloured more or less yellow in proportion to the amount present.

For the determination a weighed portion of the metal is treated as in the estimation of silicon, with the exception that a lower temperature must be employed to effect solution, as also in the evaporation of the same, and the heating until the residue becomes black dispensed with, as this would render the WO_3 insoluble in ammonia and consequently vitiate the result. The filter containing the silica and tungsten anhydride, obtained as above, is pierced, and the contents rinsed, employing as small a quantity of water as possible, into a beaker covered with strong ammonia, and digested at a gentle heat for a considerable time. This results in the tungstic anhydride entering into solution as ammonium tungstate, while the silica is not attacked, and is separated by filtering, and, if desired, may be washed, ignited, &c. The filtrate, contained in a platinum dish, is evaporated to dryness, the residual ammonium tungstate heated to redness, whereby it loses water and ammonia, resulting in tungstic anhydride being formed, and upon cooling the dish, re-weighed to determine increase due to the WO_3 containing 79.31 per cent of tungsten. Tungsten is rarely or ever present in ordinary steels or irons. Alloys of iron and tungsten are readily formed, and tungsten steel is sometimes thus made.

Oxide of Iron.

Although iron oxide is always contained in iron and steel, we are not aware of any simple and easy method, with the exception of the one now described, due to one of the authors, for its direct determination. The principle of Parry's method is that upon treating the metal containing oxide of iron with a mixture of potassium bichromate and sulphuric acid, the iron, &c., enters into solution, while the oxide of iron and silica remain unattacked. For the analysis, 10 grms. of the sample, contained in a beaker, are digested at a gentle heat (about 200° to 212° F.), with constant stirring, with 500 c.c. of a mixture of potassium bichromate and sulphuric acid—one part of the acid to six parts of a saturated solution of bichromate of potash.* When it is judged that the whole of the iron has dissolved, the solution is allowed to stand until the insoluble portions, oxide of iron and silica, have settled, when the supernatant is passed through a filter. The insoluble residue contained in the beaker is now washed three or four times with water by decantation, the washings being passed through the filter, and afterwards digested in a solution of caustic potash to remove the silica. Finally, the solution is diluted with water, passed on to the filter, the residue also being thrown on this time, the filter and contents washed three or four times with caustic potash solution, and thoroughly with water until all the alkali is eliminated. When this is effected it is removed to a crucible, ignited, and the residual oxide of iron weighed.

Titanium.

The methods employed for the determination of titanium in iron and steel are far from satisfactory. The best results are obtained by Riley's method, the *modus operandi* of which is as follows:—Six grms. of the iron or steel, contained in a porcelain dish, are treated with 100 c.c. of nitro-hydrochloric acid, until dissolved, the solution evaporated to dryness, and heated strongly. On cooling

* It has been proved experimentally that both oxides of iron are quite insoluble in this solution, and that the oxide exists in the metal as Fe_3O_4 .

the dry residue is moistened with hydrochloric acid and the solution retaken to dryness. The dish and contents are again cooled, and sufficient hydrochloric acid added to cause, with the aid of heat, solution. When this is effected it is diluted and the silica, &c., filtered off; part of the titanium is contained in the filtrate and part remains with the silica. After thoroughly washing the filter and contents, remove to a platinum crucible, ignite, and when cool mix with six times its weight of bisulphate of potassium, and fuse. Reduce the cold fused mass to a powder and extract with cold water; the titanium enters into solution, while the silica is insoluble. Separate the silica by filtration, wash, and add the filtrate to the original acid solution of the metal. The next step is to reduce the iron of the mixed filtrates, containing the whole of the titanium, from the ferric to the ferrous condition, leaving only a *very small portion* in the former condition. This is effected by means of the addition of sodium sulphite, driving off the excess of sulphurous acid by boiling. The solution is now nearly neutralised with ammonia, ammonium acetate added, boiled, the resulting precipitate of titanous acid (TiO_2) and basic acetate of iron filtered off as rapidly as possible and dried. The mixed precipitate, contained in a platinum crucible, mixed with six times its weight of potassium sulphate fused, the mass reduced to a powder, dissolved in cold water, the solution nearly neutralised, boiled for some hours, and allowed to stand in a warm place. The precipitated titanous acid is then filtered off, washed with water containing a little sulphuric acid, ignited and weighed as rapidly as possible, it being slightly hygroscopic (100 parts of TiO_2 contain 60 of titanium). Fe_2O_3 , even in very small quantities, considerably retards the precipitation of titanous acid; it is therefore expedient to add a little sodium sulphite to reduce the Fe_2O_3 contained in the solution previous to the final precipitation of the TiO_2 .

A more satisfactory method, providing a large portion of the sample be operated upon—applicable, however, only to pig irons—is as follows:—20 grms. of the iron are digested with 150 c.c. of dilute hydrochloric acid, and when the metal is nearly dissolved, 100 c.c. of the strong acid added, and the solution boiled for some time. When it is judged that all the iron has dissolved, the solution is diluted, the insoluble portion—graphite, titanium, &c.—collected on a filter, washed with dilute acid water, a solution of potash to remove the silica, and finally with dilute acid and water to eliminate the alkali. The filter and contents are then transferred to a platinum crucible and the graphite burnt off at a bright red heat. The dirty brown residue, consisting of titanium, still contained in a platinum crucible, is fused with potassium bisulphate, extracted with water, and the titanous acid precipitated as before.

Titanium is found in small quantities in pig iron, &c., but it does not appear to alloy readily with iron. Iron ores containing considerable proportions of titanium are difficultly smelted and costly to work. The resulting pig iron, although in most instances indicating only a small percentage of titanium, is, as a rule, unsuitable for the manufacture of Bessemer steel.

(To be continued).

Detection of Nitrobenzol.—J. Marpurgo (*Pharm. Post*).—The author places in a small porcelain capsule two drops of liquefied carbolic acid, three drops of water, and a fragment of potassium hydroxide the size of a pea. The mixture is carefully heated to ebullition, and the watery liquid to be examined is added. After prolonged boiling, a crimson ring appears on the margin of the liquid. If a saturated solution of chloride of lime is added, the ring becomes an emerald green. To detect nitrobenzol in soap, it is dissolved in water, mixed with an excess of milk of lime, extracted with ether, and tested as above.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 4th, 1893.

Dr. ARMSTRONG, President, in the Chair.

(Concluded from p. 251).

16. "Notes on Capillary Separation of Substances in Solution." By LESTER REED.

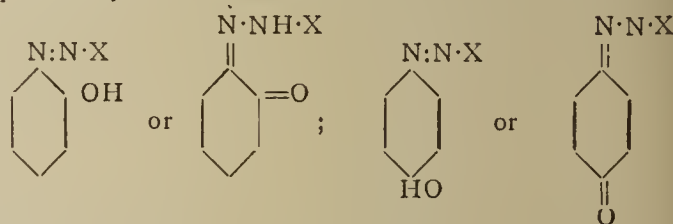
Although the separation of salts in solution by selective absorption in bibulous paper has been partly investigated by E. Fischer and E. Schmidmer (*Annalen*, cclxxii., 156—169), as I have, in ignorance of their experiments as well as of those of Schönbein, been recently investigating the same subject by a somewhat different method, I venture to briefly enumerate some of the observations I have made. My attention was first forcibly drawn to the subject by noticing the wide, colourless, very sharply defined margin which is obtained when a drop of moderately dilute solution of eosin (potassium eoside) is allowed to spread upon filter paper, although a saturated solution of eosin does not yield this margin. On adding potassium chromate to such a dilute solution of eosin, and repeating the experiment, the margin obtained is no longer colourless, but yellow, and the presence of chromate may be at once detected in this margin by touching it with a platinum wire moistened in a solution of silver nitrate, which produces a dark red spot on the yellow margin. If this yellow margin be cut off and extracted with water, a solution of potassium chromate free from eosin is at once obtained; and, conversely, eosin free from potassium chromate may be obtained if, after the drying of the drop, a drop of pure water be added and allowed to diffuse outwards from the centre; the appearance then obtained is that of a dark red central portion surrounded by a colourless margin, which is again surrounded by a yellow ring of potassium chromate, a practically complete separation or analysis of the mixture of the two salts being thus effected in a very short time. These, with a few other similar observations, are my initial facts, and naturally suggested the possibility of thus separating many other substances, as well as the use of porous media other than filter paper. I then observed that in some cases there was a very narrow colourless margin outside the yellow region of a drop of potassium chromate solution which had been allowed to spread on filter paper. At first I was inclined to suspect that this appearance was merely caused by the advancing solution crushing together and driving before it, by its expansion, some moisture already present in the filter paper. To prevent the drying of the drops during their expansion, I performed most of the experiments in an atmosphere saturated with aqueous vapour, by placing the filter paper, on which the drop lay on a small porcelain dish containing a little water, covering this with a bell jar moistened on the inside with water. When thus treated, a drop of moderately dilute solution of potassium chromate affords a most unmistakable colourless moist margin, in which silver nitrate fails to detect chromate. After this I examined in a similar way the diffusion of a mixed solution of ferric chloride and copper sulphate, testing the marginal region, after allowing about an hour for expansion, with potassium ferrocyanide, which demonstrated the existence of a marginal ring containing copper but free from iron. In the case of a solution of ammonia alum, using as tests for ammonium and aluminium respectively Nessler's test and tincture of logwood containing ammonium carbonate, no separation of the constituents was detected, both extending to the extreme limit of moisture; so that in this case I have not obtained any free water margin, and the same remark will apply to chrome alum. Employing a mixture of the

solutions of copper sulphate, ferric chloride, and ammonia alum, a beautiful separation is readily effected. Externally in this case there is a ring of pure alum detectible by the logwood test, within which is an annular zone jointly occupied by copper sulphate and alum, which is shown to be free from iron by yielding a pure chocolate colour with potassium ferrocyanide; and, lastly, a central zone where all three salts are present, and which is coloured dark blue by ferrocyanide, the lines of demarcation between these three zones being perfectly sharp and definite. In applying the logwood test by means of platinum wire, it is necessary to dry the minute spots and to compare them with similarly dried spots yielded by the same test on clean filter paper. In the absence of alum, the drops are buff; in its presence, purple. Mercuric chloride is a salt which, even in saturated solution, very readily gives a free water margin. Caustic potash or potassium iodide may be used as tests for it. In a mixture of solutions of lead acetate and mercuric chloride, sufficiently dilute to give no precipitate, the lead is observed to outstrip the mercury. Platinum chloride very readily gives a margin, the test employed being reduction by heat; in the case of a strong solution, there is a tendency to form a double margin, which suggested to me the thought either that there might be two hydrates of platinum chloride present in solution, each possessed of a different diffusibility, or else that some of the lower chloride was present. As the width of the free water margin yielded in the course of an hour or so, in some cases at any rate, depends very much on the strength of the solution, I prepared a solution of ferric chloride of such strength as to yield no free water margin, and then diluted it until a slight margin began to appear. At this point I analysed the solution, which corresponded roughly to the ratio $\text{FeCl}_3 : 200\text{H}_2\text{O}$. On continuing the dilution in geometrical progression by continuously halving its strength, the free water margin rapidly increased in diameter, being always, however, separated from the iron region by a sharp line. When a dilution in the ratio of about $\text{FeCl}_3 : 30,000\text{H}_2\text{O}$ is reached, the iron seems to have almost lost its power of diffusing, getting little, if at all, beyond the space wetted by the drop when it first falls upon the paper. Of course, at this dilution it may be said that we are no longer dealing with ferric chloride, but with the products of its dissociation; and this explanation might be adequate but for the fact that an extremely dilute solution of sulphuric acid behaves in the same way. A drop of ferric chloride solution, while spreading upon filter paper, frequently presents an appearance, more or less noticeable, of concentric rings, suggesting, perhaps, the presence of more than one hydrate in solution. Imagining that the presence of hydrates in solution might be in some way or other connected with the formation or diameters of these free water margins, I prepared a solution of potassium bichromate corresponding in strength to Guthrie's cryohydrate, viz., $\text{K}_2\text{Cr}_2\text{O}_7 + 292\text{H}_2\text{O}$. It readily yielded a margin of water, and it is remarkable that this margin is of about the same width as that yielded either by a saturated, or by a very much more dilute, solution of the salt. I continued the dilution of this solution in geometrical progression, as with ferric chloride, until I brought it to $1/128$ th of the strength of the cryohydrate, but even this great dilution had little or no effect on the diameter of the free water margin, a result notably differing from that obtained in the case of ferric chloride or sulphuric acid. Copper sulphate solution, on the other hand, undergoes great change in diameter of free water margin on dilution. Hence it may be enquired whether a change in the diameter of free water margin, which must obviously represent a change in the relative velocities of water and the dissolved substance, may not in all cases be an evidence either of dissociation or of changes in the composition of the hydrates existing in solution. Sulphuric acid yields beautifully definite results, the test relied on being that of drying the filter paper at a high temperature, when the portion over which the acid has extended chars. A free water margin

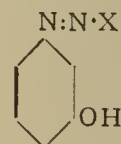
begins to be formed at about the strength of 1 part of acid by volume to 200 parts of water; and when a dilution of about 1 in 4000 is reached, the acid (as was the case with ferric chloride) seems to have almost totally lost its power of diffusing, and yields a relatively enormous free water margin. It would be very interesting if it could be shown that this inner zone of non-diffusible sulphuric acid represents a definite hydrate, the diffusibility of which is arrested by its enormous molecular weight, perhaps approaching those of such non-diffusible colloidal substances as the albumenoids; and such a hydrate might possibly be at or near the extreme limit of possible hydration of the acid. With regard to the employment of porous media other than filter paper, I have obtained satisfactory results, both with the mixture of potassic chromate and eosin, and with that of ferric chloride and copper sulphate, by using tubes containing powdered kaolin lightly rammed down, upon the top of which the solution was placed and allowed to soak downwards. I had hoped that this method of separation, or some modification of it, might have proved available for the separation of alkaloids from organic matters of different nature, with a view to their subsequent identification, but have hitherto been very partially successful in this direction.

17. "Note on a Meta-azo-Compound." By R. MELDOLA and F. B. BURLS.

While azo-compounds of the ortho- and para-series can be represented either as hydrazones or as true azo-compounds by the formulæ—



the azo-derivatives of the meta-series—



cannot be formulated as hydrazones. We have commenced a series of experiments having for their object the preparation of members of the meta-series, in order to institute a comparison between their properties and those of the ortho- and para-series. It is obvious that a comparative study such as we propose to undertake is calculated to throw light on the question of the constitution of organic colouring matters, as the "quinonoid" bonds are not present in the meta-compounds according to our present method of formulation. As the work must be for the present interrupted, owing to one of us (F. B. B.) having accepted an appointment away from London, we desire to place our results on record in this preliminary communication.

The first compound with which we experimented has not given a decisive result on account of certain practical difficulties which we have not yet succeeded in overcoming. The only satisfactory compounds which are worth studying from the present point of view are evidently those of the type—



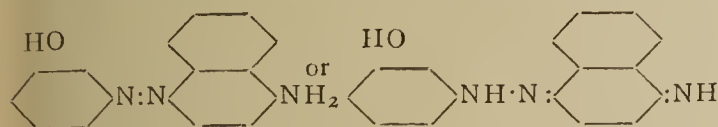
in which X is an *unsubstituted* hydrocarbon radicle. Metamidophenol was diazotised in presence of chlorhydric acid in the usual way and combined with α -naphthylamine, also dissolved in chlorhydric acid. The mixture of the two solutions gradually became of a deep violet-red colour. The azo-compound was finally precipitated by the addition of sodium acetate. The precipitate was collected, washed with water, and purified by dissolving it in cold dilute caustic soda, filtering and reprecipitating by acetic acid; it was then digested with

dilute ammonia, washed with water, and crystallised alternately from dilute alcohol and benzene. Analysis showed that the substance was pure.

Calculated for $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$: C, 73.03; H, 4.94; N, 15.96.

Found: C, 73.10 and 73.14; H, 5.56 and 5.54; N, 15.94.

Metaphenolazo a naphthylamine may be fairly assumed to have the constitution expressed by the formula—



It crystallises in dull, orange-coloured needles fusing at 106° . Its solution in all solvents is orange coloured and it possesses strong tinctorial power as an orange dye-stuff. It is both acid and basic in properties, readily dissolving in cold aqueous solutions of alkalis, forming orange-coloured liquids and also forming well defined salts with acids. The solutions of its salts are of a magnificent violet colour. If the hydrazone formula be assigned to the compound, it must be assumed that contact with acids causes its transformation into a compound of the azo-type, as the molecule is strongly basic towards acids and the presence of the anido-group is indicated by the readiness with which the compound can be diazotised. It dissolves in strong sulphuric acid, forming a dull magenta-red coloured solution, becoming violet on dilution, and on the further addition of water the sulphate separates out in bronzy crystals. Of the salts, the hydrochloride was specially examined. This was prepared by dissolving the base in boiling alcohol and adding strong chlorhydric acid; the colour of the solution changes from orange to violet; the hydrochloride separates out on cooling. The salt forms flat needles having a beautiful bronzy lustre. A specimen allowed to dry in the air for some time and then for a day in a vacuum gave the following results on analysis:—

Calculated for $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$: Cl, 11.18; N, 13.22; H_2O , 5.67.

Found: Cl, 11.36; N, 13.1; H_2O , 5.73.

The salt does not part with its water at temperatures below 110 — 120° , and the loss of the water molecule is accompanied by a change in colour from a metallic bronze to a dull green.

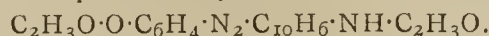
In order to further characterise the azo-compound, the acetyl derivative was prepared by boiling a solution of the substance in glacial acetic acid with acetic anhydride till the original violet colour of the solution had changed into orange. On precipitating with water and crystallising the product from dilute alcohol, it was discovered by analysis that it probably consisted of a mixture of a monacetyl with a diacetyl derivative; this was confirmed by the observation that the compound did not completely dissolve in dilute caustic soda, but left a slight residue. Purification was effected by this means, and the dissolved (phenolic) portion, having been precipitated by chlorhydric acid, was crystallised from dilute alcohol and then from dilute acetic acid till the melting point was constant. Beautiful golden scales were thus obtained melting at 232 — 235° , and giving on analysis results agreeing with the formula of the monacetyl derivative—

Calculated: C, 70.81; H, 4.91; N, 13.77.

Found: C, 70.53; H, 5.23; N, 13.70.

As this compound is phenolic, it is clear that the acetyl displaces amidic hydrogen, and, therefore, that the product has the formula $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{C}_2\text{H}_3\text{O}$. It dissolves in alkali, forming an orange-coloured solution and possesses strong tinctorial properties. The non-phenolic derivative was not formed in sufficient quantity to enable us to obtain sufficient for complete examination. The melting point, after several crystallisations from

dilute alcohol and benzene, was about 226° , and the nitrogen approximated in quantity to that required by the diacetyl derivative. The substance forms flat needles of a golden colour, and is also an orange colouring matter. As it is non-phenolic, the hydroxylic hydrogen is probably displaced as represented by the formula—



The main object of the present investigation could not be realised in this case owing to the impossibility of displacing the NH_2 group by H. The method usually adopted in such cases was tried under various conditions, but the product was always a brown uncrystallisable resinous substance, which could not be purified by any artifice so as to give satisfactory results on analysis. The substance was phenolic and dissolved in alkali, forming a brown coloured liquid. It may have contained the naphthaleneazometaphenol sought for, but in its impure condition we could draw no conclusion with respect to its colour properties. The experiments are therefore being extended to other compounds of the same series.

18. "The Influence of Moisture in Promoting Chemical Action." Preliminary Note. By H. BRERETON BAKER, M.A.

It has been shown by the author (*C. S. Trans.*, 1885; *Phil. Trans.*, 1888) that when moisture is removed as completely as possible, certain substances, e.g., carbon, sulphur, phosphorus, &c., can be heated in an atmosphere of oxygen without undergoing visible combustion; and he has been engaged during the last two years in continuing the investigation, with the object of ascertaining in what way moisture promotes chemical action. One of the cases which he has studied is the formation of ammonium chloride from ammonia and hydrogen chloride. A difficulty presented itself at the outset in drying ammonia gas, as it is absorbed by phosphoric oxide; this was overcome by drying the gas as completely as possible by freshly ignited lime, after which it was found that phosphoric oxide did not absorb any appreciable quantity. Hydrogen chloride was dried in a similar way by sulphuric acid, and finally by a week's contact with phosphoric oxide. On allowing the dried gases to mix, *no ammonium chloride fumes were produced*, and no contraction was indicated by the mercury gauge attached to the apparatus; and it may therefore be concluded that ammonia and hydrogen chloride do not combine when dry. On introducing a small quantity of moist air, union at once takes place, however. In like manner, sulphur trioxide was found not to unite either with lime or barium monoxide or copper oxide. Furthermore, no brown fumes were produced on mixing dry nitric oxide with dry oxygen. The author is engaged in studying the effect of moisture on various types of chemical action, and he hopes soon to be able to communicate the results to the Society.

*19. "The Genesis of New Derivatives of Camphor containing Halogens by the Action of Heat on Sulphonic Chlorides." By F. STANLEY KIPPING, Ph.D., D.Sc., and W. J. POPE.

When the sulphonic chlorides described in a recent paper are heated at temperatures not very far above their melting-points, they undergo decomposition, sulphur dioxide being evolved. In the case of camphorsulphonic chloride, chlorocamphor is produced, in accordance with the equation $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\text{Cl} = \text{C}_{10}\text{H}_{15}\text{OCl} + \text{SO}_2$; at the same time a considerable quantity of an oil is formed, the nature of which remains to be determined. This chlorocamphor separates from cold dilute alcohol in arborescent forms; it melts at 137 — 138° ; analyses gave C=64.26, H=8.47, Cl=19.35; $\text{C}_{10}\text{H}_{15}\text{OCl}$ requires C=64.37, H=8.04, Cl=19.09.

By heating chlorocamphorsulphonic chloride, a well-defined dichlorocamphor is obtained, which crystallises from light petroleum in long prisms melting at 118° to 119° ; like the sulphonic chloride from which it is derived it is dextrorotatory, its specific rotation in chloroform

solution being a little higher than that of either of the known dichlorocamphors, namely, $[\alpha]_D = 85^\circ$. Analyses gave C=54.27, H=6.66, Cl=31.84 and 32.04; $C_{10}H_{14}OCl_2$ requires C=54.34, H=6.34, Cl=31.99.

The compound prepared from bromocamphorsulphonic chloride closely resembles dichlorocamphor, and crystallises from light petroleum in lustrous prisms melting at 142° — 143° ; like the latter, it has a high specific rotatory power, namely, $[\alpha]_D = 104^\circ$, in chloroform solution.

These three derivatives of camphor appear to be different from any known compounds, and their further study will, it is hoped, throw light on the complex question of isomerism in the camphor series; it is possible that, starting from the corresponding sulphobromides, it will be possible to obtain new bromo-, dibromo-, and bromochlorocamphor derivatives, and in this way to establish fresh cases of isomerism; experiments with this object in view are in progress.

Dr. Armstrong informs us that Dr. Wynne and he have noticed in the course of their studies of naphthalene derivatives that a number of sulphochlorides undergo decomposition when heated above their melting-points, and that Dr. Wynne has observed that the sulphochlorides of some of the chlorinated toluenes behave similarly. The study of the behaviour of sulphochlorides and allied compounds generally when heated is therefore desirable, and will be carried on in the Central Institution laboratory.

NOTICES OF BOOKS.

Chemistry for All; or, Alternative Elementary Chemistry in Accordance with the Syllabus of the Department of Science and Art. By W. JEROME HARRISON, F.G.S., Chief Science Demonstrator for the Birmingham School Board, and R. J. BAILEY, Assistant Science Demonstrator. London, Glasgow, Edinburgh, and Dublin: Blackie and Son, Limited, 1893. Small 8vo., pp. 150.

WHAT "alternative elementary chemistry" may be might puzzle the "intelligent foreigner" of whom we have formerly read. If more treatises on elementary chemistry are needed, which we can scarcely admit, they might better be in accordance with the latest discoveries than with any "syllabus."

The work before us certainly contains no errors, but it is typically "departmental" and examinational. It is strange that the heads of the "department" never, when seeking for the causes of our difficulty in competing with Germany in the chemical arts, reflect that the course of instruction there given is not examinational.

The Earth: Evolution of Life on its Surface, its Past, its Present, and its Future. (La Terre, Evolution de la Vie a sa Surface, son Passé, son Présent, son Avenir). By EMMANUEL VAUCHEZ. In Two Volumes. Second Edition, 1893. 8vo., pp. 769. Paris: C. Reinwald and Co.

THE author of the work before us is unquestionably an evolutionist and a Darwinian, in as far as he refers the origin and the development of species mainly to the "struggle for existence." He sets out with a general survey of our earth as a member of the group attendant upon the sun. He then proceeds to the origin of the solar system, the primitive fire-mist, the nebulae observed in the heavens and photographed, and the successive birth of the planets. But whilst ably and eloquently describing the formation of nebulae, suns, and planets, he says not a word on the genesis of the elements, as the material from which nebulae, suns, and planets must ultimately have been derived. His views on this subject

would have possessed a very high interest. Are the elements primordial, or have they been gradually evolved? He suggests, however, that in the præ-geological ages, at the time when the earth was a sun, the chemical elements themselves were dissociated. But had they ever been associated?

Life, and even thought, the author regards as a mere modification of force.

In discussing the origin and the development of life, M. Vauchez has the courage—still too rare in France—to reject the catastrophism of Cuvier. The account here given of microbia, of their signification, and of the part which they play, is fully on a level with the present results of research.

The remarks on the evolution of human civilisation, suggestive as they are, and humiliating as they must appear to modern "progressives," lie too far from the scope of the CHEMICAL NEWS for a critical analysis.

The different modifications of energy are here regarded as reducible to electricity.

An especial consideration is given in the first chapter of the third part to infection, to which no objection can be taken. But when M. Vauchez assigns an extinct anthropoid as the ancestor of mankind, and mentions an existing ape as making use of fire, we fear he is going beyond what has been demonstrated.

In the fourth part, treating of diet, the author considers that vegetarianism will in the future force itself upon mankind, and awaits from this change a physical and moral amelioration of our race! He does not seem to look forward to the synthetic production of food.

In the second volume the author goes back to consider gases, which, we submit, might have been more appropriately studied in an earlier part of the work.

The remainder of the author's studies fall entirely beyond our scope. Hypnotism, the history of religion, necromancy, metempsychosis, are subjects which we cannot discuss.

This work gives proof of extensive learning and of remarkable fertility and suggestiveness of thought; and to those able to use it aright it will prove valuable.

CORRESPONDENCE.

THE CHICAGO EXHIBITION.

To the Editor of the Chemical News.

SIR,—The New York Section of the American Chemical Society (Morris Loeb, Secretary, University of the City of New York, Washington Square, East, Room 16) will be happy to contribute, by all possible means, to the comfort and enjoyment of the foreign chemists who may visit New York on their way to or from Chicago during the World's Fair.

Visitors are requested to leave their names and addresses with the Secretary of the Reception Committee, who will also be glad to furnish all information at his command in reply to letters of inquiry.—I am, &c.,

(For the Reception Committee),

H. CARRINGTON BOLTON.

OXIDATION PRODUCTS OF GLUCOSE.

To the Editor of the Chemical News.

SIR,—Mr. Langmuir consulted practical manuals about a question which has as yet no practical importance. As I happened to be in the library of Columbia College when I read, dated from that College, an inquiry as to the products of oxidation of glucose by Fehling's solution, I thought I would see whether this excellent library really

lacked the desired information. An English translation of Strecker-Wislicenus mentions "tartronic and other acids" as the products. Beilstein gives full particulars. Both these books stand among the works of general reference, and it is therefore particularly easy for any one to consult them. But had the questioner traversed the few feet necessary to read the answer to his inquiry, he would have lost the satisfaction of knowing that, by the time he reads this, question and answer will together have travelled 12,000 miles.—I am, &c.,

A. E.

New York, May 15, 1893.

OXIDATION PRODUCTS OF GLUCOSE.

To the Editor of the Chemical News.

SIR,—Most chemists will agree with your correspondent, Mr. A. C. Langmuir (CHEM. NEWS, lxvii., 204), that it is surprising that the products of the reaction of Fehling's solution on glucose should not have been more completely studied. In the absence of more exact information I may quote the following passage ("Commercial Organic Analysis," i., 225):—

"The action of reducing sugars on Fehling's solution is not precisely known, but among the products are:—1. Acetic and formic acids. 2. Certain non-volatile acids, especially tarttronic, an acid forming uncrystallisable salts, and an acid decomposed with formation of humus-like products on heating its alkaline solution. 3. A gum-like substance."

I cannot now trace the source of this information, but believe it was derived from an abstract published in the *Journal of the Chemical Society* prior to 1882.

Of course it is well known, through the researches of Soxhlet and others, that the reaction between glucose and the alkaline cupric solution is far from constant, and that to ensure really accurate results a series of approximating experiments must be made.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, May 27, 1893.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 19, May 8, 1893.

New Type of Phosphorites.—Armand Gautier.—In these phosphates the aluminium salt preponderates. It is soluble in the cold in weak alkaline lyes, and to a large extent in ammoniacal ammonium citrate. Although the phosphoric acid is divided almost equally between the calcium and aluminium, these two phosphates are only associated or very feebly united.

Remarks on the Specific Heat of Carbon.—H. Le Chatelier.—The specific atomic heat of graphite (retort coke) increases from 250° to 1000° in a manner strictly proportional to the temperature. The coefficient of increase is much more considerable than it seems to result from the experiments of Weber.

The Flames of Some Metals.—Denys Cochin.—The compounds of the alkaline and alkaline-earthly metals, when volatilised in flames, yielded the first known spectra. These spectra in the visible portion are not identical with those obtained in making use of electricity as the source of heat. It seemed to me that it was interesting to examine how they terminated on the side of the most refrangible radiations, in a region where we

have a great number of photographs of electric spectra, but no flame spectra. I have succeeded in photographing the spectra of coloured flames by the aid of a spectro-scope of two quartz prisms of inverse rotations, with lenses of quartz and spar, according to M. Cornu's arrangement (*Journ. de Phys.*, vol. viii. (1879), p. 185). The frame of the dark chamber, which serves as an eyepiece, is slanting as in most spectrographs, and it is provided with a cylindrical bottom upon which steel springs apply exactly a flexible plate (Eastman's film). The sensitive preparation is then quite entire in its focal surface, which is a cylinder with a base nearly hyperbolic. The bottom of the frame has been brought to this form by approximations. The time for exposure is very long, half an hour to an hour. It is shorter if we use the flame of hydrogen as a source of heat. The results are approximately the same in each case. We always obtain the bands of the vapour of water $\lambda = 309$, &c., and we have never been able to obtain the metallic rays situate below at least without further prolonging the experiment. The rays are identified by comparison with those of an electric spectrum produced by means of the sparks of a Leyden jar, striking between the poles of cadmium, aluminium, &c., for about a minute. They are prevented from covering all the height of the flame spectrum by means of a small perforated screen, placed on the slit, which limits the spectrum for comparison to a small height. The following results were obtained:—

Alkaline Metals.

Lithium.— $\lambda : 413$.

Sodium.—Double ray $\lambda : 330.3$ and 330.2 , mentioned by MM. Kayser and Runge as obtained with the electric arc.

Potassium.—Rays $\lambda : 404$ and 344.4 .

Rubidium.—Visible ray $\lambda : 420$, and besides, by employing the flame of hydrogen, two twin rays distinguished by Kayser and Runge as $\lambda : 359.355.7$ and $335.334.8$.

Cesium.—Besides the visible blue rays $\lambda : 459.7450$, we obtain the invisible rays $\lambda : 388$, $\lambda : 361.5$, and $\lambda : 347.75$.

Alkaline Earthy Metals.

Calcium.—Visible ray $\lambda : 422.6$. The exposure was prolonged with the flame of hydrogen for seventy-five minutes without obtaining the image of any invisible calcium ray, not even of the ray HH'. Nevertheless, the bands of watery vapour, $\lambda : 309$, and three bands beyond them, likewise due to vapour of water, have been photographed.

Strontium.—Visible ray $\lambda : 460.7$.

Barium.—Visible ray $\lambda : 487$. Ultra-violet rays have not been obtained for any of these three metals.

Thallium.—Two invisible rays, situate respectively to the left of the rays 10 and 9 of cadmium at $\lambda : 353$ and 378 . The existence of these three rays in the flame spectrum approximates thallium to the alkaline metals.

Attempt at a General Method of Chemical Synthesis.—Raoul Pictet.—This paper will be inserted in full.

Basicity and the Functions of Manganous Acid.

—G. Rousseau.—Under certain conditions manganous acid is capable of saturating 2 mols. of a diatomic base like calcium, but we cannot conclude that it presents the characters of a normal tetrabasic acid. The 2 mols. are not combined in the same manner. The first alone corresponds to two acid functions, the saturation of which produces stable salts of the type CaO, MnO_2 . The second, which unites with MnO_2 only in strongly basic media, corresponds to two alcoholic functions. Hence we see that manganese dioxide should rank with the alcohol-acids, being in reality a bibasic acid with a complex function. The existence of the compound $2\text{CaO}, \text{MnO}_2$, a derivative of the unknown hydrate $\text{Mn}(\text{OH})_4$, establishes the tetravalence of manganese.

Constitution of Licareol.—Ph. Barbier.—This paper consists chiefly of diagrammatic formulæ.

Syntheses with Aluminium Chloride.—P. Geniesse.—In syntheses with aluminium chloride, we may obtain at once the formation of the normal and of an iso-compound. The production of the former is favoured by the use of a relatively small quantity of aluminium chloride.

On a Liquid Isomer of Hydrocamphene.—L. Bouveault.—The liquid in question, $C_{10}H_{18}$, is colourless, having a faint scent of essential oil of orange, and boils at 148° — 149° . Its vapour density leads to the molecular weight 138.2. Hydrocamphene, on the contrary, boils at 157° — 158° .

Chemical Composition of Oil of Niaouli.—G. Bertrand.—The niaouli (*Melaluca vividiflora*) is a myrtaceous tree abounding in New Caledonia. Leaving secondary products out of the question, the author concludes that this essential oil (besides a dextrorotatory turpentine, $C_{10}H_{16}$), consists of a mixture of three bodies, eucalyptol, a carbide boiling at 175° (probably citrene), and a terpinolol.

Systematic Glass-Moulding.—Léon Appert.—The author's procedure requires to be described in detail. It can scarcely be placed under the heading "chimie industrielle" when the author himself informs us that the process is "purely mechanical."

Bulletin de la Société Chimique de Paris.
Series 3, Vols. ix. and x., No. 8.

This number contains no original matter.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Grinding and Polishing Quartz.—I shall be much obliged if any of the readers of the CHEMICAL NEWS will refer me to some book where I can obtain instruction in grinding and polishing quartz plates and prisms. I am making some small pieces of apparatus of quartz, and should prefer to grind and polish them myself rather than get them done elsewhere. What I more particularly want to know is the material on which to grind, e.g., iron, plate-glass, or stone, and the powders to use, whether emery, putty-powder, or rouge.—AMATEUR.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Society of Chemical Industry, 8. "The Movement of Air as Applied to Chemical Industries," by H. G. Watel. "New Cellulose Derivatives and their Industrial Applications," by C. F. Cross and E. J. Bevan.

— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 6th.—Royal Institution, 3. "The Waterloo Campaign," by E. L. S. Horsburgh, M.A.

WEDNESDAY, 7th.—Geological, 8.

THURSDAY, 8th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Mathematical, 8.

— Royal Institution, 3. "The Geographical Distribution of Birds," by R. Bowdler Sharpe, LL.D.

FRIDAY, 9th.—Royal Institution, 9. "The Recent Solar Eclipse," by Prof. T. E. Thorpe, D.Sc., F.R.S.

— Physical, 9. "A New Photometer," by A. P. Trotter. "Notes on Photometry," by Prof. S. P. Thompson, F.R.S. "The Magnetic Field near a Wire," by Prof. G. M. Minchin, M.A.
— Astronomical, 8.

SATURDAY, 10th.—Royal Institution, 3. "Falstaff": a Lyric Comedy by Boito and Verdi, by Dr. A. C. Mackenzie.

ERRATUM.—On page 253, col. 2, in the paragraph headed "Identity of Cystine and Ulexine," *cytisine*, the alkaloid of *Cytisus laburnum*, is erroneously printed "cystine," which is an entirely different substance.

TO CORRESPONDENTS.

B. Taylor.—"Workshop Receipts," published by Spon.

J. Clegg.—After india-rubber has been vulcanised it cannot be dissolved off so as to be subsequently useful. You can dissolve the iron from the india-rubber by means of dilute sulphuric or hydrochloric acid.

W. D.—It is impossible to acquire a proper knowledge of chemistry without experimental practice in a laboratory. Any small room with a sink and a chimney in it can be used at first as a laboratory, and the necessary apparatus to begin with need only cost a trifle. Start with a small book on practical chemistry, and avoid theory at first. A useful book to begin with will be "Thorpe's Qualitative Chemical Analysis," published by Longmans, Green, and Co.

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CHEMISTRY FOR ALL: In Accordance with the Syllabus of the Department of Science and Art. By W. J. HARRISON, F.G.S., and R. J. BAILEY.

London: BLACKIE and SON (Limited), Old Bailey.

THE CHEMICAL NEWS.

VOL. LXVII., No. 1750.

ASSAY OF TIN ORE.

By THOMAS MOORE.

HAVING recently had occasion to make some enquiries into the different results obtained in the assays of tin ore, I was naturally led to look up and repeat some of the processes at present generally in use with a view of ascertaining wherein lay the sources of error, if any.

The first difficulty to be overcome is the satisfactory decomposition of the mineral. Some authors advise that the ore, *i.e.*, cassiterite, be treated with acid to extract as much soluble gangue as possible. At first sight this seems to be rather a risky proceeding, and accordingly the following experiments were instituted:—Five samples, each of 5 grms., were well boiled with aqua regia; three of them were then somewhat diluted with water and then filtered, the filtrate evaporated to dryness, and the residue, after fusion with dried sodic thiosulphate, dissolved in water and filtered. The filtrate was then acidulated with hydrochloric acid, and the precipitate so obtained boiled with strong hydrochloric acid to dissolve any stannic sulphide present. A piece of zinc was then added and allowed to dissolve completely in the cold, the solution again boiled to dissolve any metallic tin, and then tested with mercuric chloride and a solution of gold, neither of which gave any reaction. The remaining two samples were then evaporated to dryness, and the residue extracted with water. The solution treated as already indicated gave also no reaction for tin. It may therefore be safely assumed that the preliminary treatment with aqua regia does not cause any loss of tin; this is a point of considerable importance, as the presence of other elements only serves to complicate the remainder of the assay.

The method of fusion with dried sodic thiosulphate gives a complete decomposition if the mixture is kept fused for at least one hour; a shorter fusion than this gave in a few instances an undecomposed residue. The sulphide precipitate from the solution of the melt by hydrochloric acid is largely mixed with free sulphur, and exhibits a disagreeable tendency to creep over the edge of the filter and also to give a cloudy filtrate. The addition of ammonia acetate to the wash-water corrects this to a certain extent.

The method of Hallett was also tried. Four fusions were made, and in each case the solution was complete. The expulsion of the hydric fluoride is a serious drawback and occupies a considerable time.

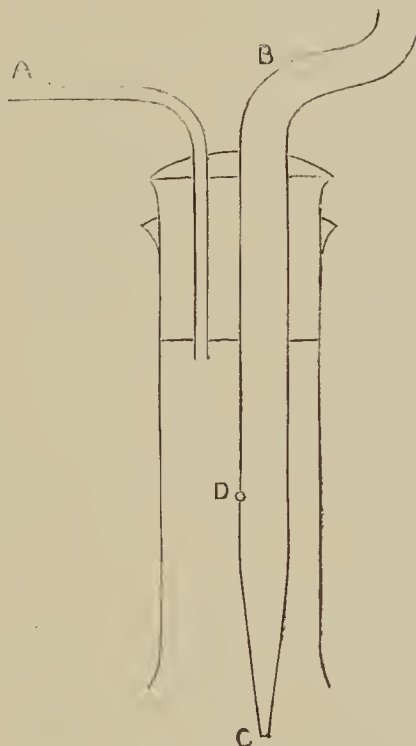
The potassic cyanide proceeding has already been submitted to searching tests by Hofmann and others, so that there seemed nothing more to be done in connection with it.

The reduction of the mineral by zinc, as proposed by Wells, was then experimented with. This method consists in mixing the ore with zinc dust, and treating with hydrochloric acid, whereby the tin is reduced to the metallic state. This seemed to be a very feasible and ingenious way of attacking the problem, and, indeed, on trying the experiment it was found that the tin was rapidly reduced, and that on removing the reduced metal and repeating the treatment with the undecomposed residue, the reaction seemed to have been complete. Unfortunately, however, the sponge of tin, on being dissolved in hydrochloric acid, was found to contain enclosed ore particles, which settled to the bottom of the beaker glass as a heavy sediment.

The reduction was also tried by electricity by covering

the mineral in a platinum basin with dilute sulphuric acid, inserting an electrode into the liquid, and connecting the basin to the pole of a galvanic battery, but with no better results; the sponge becomes inflated with the evolved hydrogen, and floats to the surface charged with particles of ore beyond the sphere of chemical action. Still the idea of reduction with metallic zinc seemed too good to abandon, and I therefore resolved to try its action in the dry way, and, after the inevitable failures, at last succeeded in the following manner:—

A porcelain crucible of from 10 to 15 c.c. capacity is taken, and a layer of zinc powder placed on the bottom of it; on this there is placed a mixture of 0.5 gm. of the ore with 5 or 6 grms. zinc powder, and over this another thin layer of the powder, and a solid well-burned piece of charcoal to keep a reducing atmosphere and to prevent the lid becoming cemented to the sides, and so giving rise to an explosion. The charged crucible is now placed in a red-hot muffle, and left there until the burning vapour of zinc has almost ceased; the crucible is then removed from the muffle, and allowed to cool without removing the lid. The combustion of the zinc vapour gives rise to the



formation of a tube of oxide of zinc (presenting a very curious appearance), which, when dissolved in dilute acid, gives no trace of tin. The piece of charcoal is then removed, and the crucible and its contents treated with hydrochloric acid; after the first violent effervescence due to the excess of zinc is over, the sponge of tin is dissolved by boiling the liquid for a few minutes. The insoluble residue of silica, &c., will be found to be quite free from tin. The zinc powder used in this process must be quite free from lead, and is best prepared by triturating some melted zinc in a hot iron mortar, and separating the coarser particles with a fine sieve. The product so obtained is much coarser, but far purer, than the ordinary zinc dust.

Having obtained a solution of the ore, a variety of methods have been proposed for the estimation of the tin it contains. To precipitate the tin by metallic zinc, and weigh it as such, has never given good results in my hands, as the filtrate invariably contains notable quantities of the metal, even when the solution from which it was precipitated was but slightly acid; when the solution is rendered nearly neutral, then the filtrate is free from tin, but, on the other hand, the sponge is contaminated with either oxide or a basic salt of zinc.

Turning to the volumetric methods the choice seems to

lie between the iodine process in alkaline solution or indirectly with an iron solution and potassic bichromate or permanganate in an acid liquid. Both procedures have yielded excellent results with pure materials, but with solutions containing, as they usually do, much zinc and free hydrochloric acid, the final reactions leave much to be desired. The utmost care must be taken to prevent access of air to the stannous solution, and, in diluting, only recently boiled distilled water is admissible. In this respect those processes involving the reduction of a ferric salt have this advantage, that the acid ferrous liquor may be exposed to the air for a comparatively long period without any appreciable difference. The direct titration of the stannous solution with potassic bichromate is not to be recommended, for, as first pointed out by Mohr, they are capable of existing together in the same liquid without decomposition.

Recognising these difficulties, and with the intention of devising a method whereby the solution of the reduced tin might be directly titrated, I attempted to apply the principle of the reduction of cupric to cuprous chloride by stannous chloride,—in fact, reversing the well-known process for the estimation of copper. It was soon apparent, however, that the eye could more readily distinguish the disappearance of the yellow tint than the first faint traces of its appearance, and, moreover, the presence of suspended matter in the liquid still more obscured the change. After a number of experiments the following course was at last adopted:—

Dissolve the sponge in hydrochloric acid in a flask through which a current of CO_2 circulates, add to the hot solution a known quantity of ferric chloride solution, allow to cool, and filter rapidly by suction; then titrate the excess of ferric chloride with cuprous chloride (Winckler's process) with KC_2S as indicator, and from the amount of iron reduced the tin contents may be easily found.

The advantages gained by titration with cuprous chloride are, that the large excess of zinc chloride does not affect the reaction, neither does the presence of iron, which is, of course, already present as a ferrous salt. The flask in which the solution takes place is fitted with a doubly perforated cork containing two glass tubes. The tube A is connected to a CO_2 apparatus; B is of larger diameter, and is gradually drawn to a narrow tube at C. About an inch above this in the wide part a small orifice is blown (D); the object of this hole is for the escape of the CO_2 , &c., so that when the ferric chloride is run into the solution by placing the tip of the pipette at D, the liquid clinging to the sides of the tube drops into the inside of the flask from the point C, thus avoiding being blown back in the tube, and at the same time preserving a non-oxidising atmosphere in the interior. Such an arrangement is exceedingly useful in the distillation of liquids, as in the Kjeldahl process, and effectually prevents any of the solution being carried over into the distillate.

Unfortunately, however, in the course of analysis tin is generally separated as the stannic sulphide, or at least in a stannic condition, in which state the volumetric methods are not available, so that if they are to have any technical value some rapid and simple process must be applied for the reduction of the stannic chloride, without, if possible, reducing the tin to the metallic state, and re-dissolving with all its incidental inconveniences. Boiling with metallic copper cannot be applied owing to the formation of cuprous chloride, which reduces the ferric chloride; metallic iron is also efficacious, but loads the solution with a ferrous salt, and the same applies to nickel and cobalt. Metallic lead, however, gives a perfect reduction without at the same time precipitating any tin. The solution should be concentrated to a small volume, and contain about one-fourth of its bulk of strong hydrochloric acid; 5 or 6 grms. of grain lead are then added, and the flask gently heated on the water-bath for a couple of hours, or raised nearly to the boiling-point for fifteen minutes. If too much hydrochloric acid is added, there will be a copious formation of

chloride of lead crystals; this, however, does not interfere with the reduction. The liquid is now poured into an excess of ferric solution, and the residual lead and its chloride washed by decantation, after which it only remains to titrate the unreduced iron with cuprous chloride.

The results of a large number of trials with samples of known percentage were very satisfactory, and the time required for the assay need not exceed one hour—indeed, when everything is in readiness, not more than half that time is necessary.

Noumea, New Caledonia.

ON THE ANALYSIS OF PIGMENTS WHEN GROUND IN OIL.

By J. B. HANNAY, F.R.S.E., F.I.C.

IN preparing a pigment for analysis by separating the solid material from the oil in which it is ground, much trouble and loss of time sometimes occurs owing to the peculiar behaviour of the oil. With moderate quantities of most solvents the oil does not form a true solution, but a mixture standing midway between a solution and an emulsion, which so affects the contained solids that the mixture is extremely difficult to filter.

With solvents such as chloroform or bisulphide of carbon, which have a high density, it is very difficult to obtain a clear filtrate, and the separation of the oil is a tedious operation; but with fluids of lower density, such as benzene or ether, results may be obtained which leave nothing to be desired.

When entering upon the work it was necessary to clear a number of fallacies out of the way—and one especially, which had obtained a very firm hold on the literature of pigments. It has been long held that the oil in which the "Dutch" white-lead (basic carbonate) is ground forms some combination or "saponification" with the lead—forming, indeed, "lead soap." In a paper by Mr. Leighton and myself (*Proc. Chem. Soc.*, May 4, 1893), it has been clearly shown that in no case is there the slightest action between white-lead and oil, but that they simply mix mechanically as do all other pigments.

Were not this the case, the analysis of white-lead in oil would be a difficult and uncertain operation; but after devising tests which detect one part of oleate of lead in a million of pigment, it was shown that in no case is there found any oleate or similar compound due to the action of the oil.

The point in technical analysis which I am about to emphasise needs this preliminary explanation, as I find that the belief in saponification of oil by white-lead is not confined to ignorant tradesmen, but has been adopted by professional chemists. Lately, one chemist (Harland, *Journ. Soc. Arts*, xxiv., March, 1893) stated that he had examined hundreds of samples of white-lead, in all of which he found combination between the white-lead and the oil; and he has since affirmed (*Proc. Chem. Soc.*, May 18, 1893) that it is impossible to wholly remove the oil from an ordinary white-lead paint by means of ether.

How, then, does this chemist analyse his samples of white-lead, and does he report on the percentage of oleate of lead present? In contradiction of these statements, I assert that no oleate of lead or other lead compound is ever formed when white-lead is mixed with linseed oil, and that it is possible to absolutely free white-lead or any other pigment from oil by many solvents, but that this can be done with greatest ease and rapidity by using the method I am describing.

The peculiar property of the solution of oil to which I have referred may be entirely obviated by a very simple precaution. The emulsifying or structural property of the oil is entirely destroyed by the addition of a large

volume of methylated ether, and instead of having an emulsified liquid difficult to filter, the pigment separates at once from the liquid, and settles to the bottom in flakes like a miniature snow-storm. The only points to be observed are, that the methylated ether must be fresh and contain its quota of methyl ethyl ether (as re-distilled ether tends to form the emulsion), and it must be added in very large excess—something approaching 100 c.c. to every grm. of the pigment. On shaking this up with the pigment, very rapid solution of the oil takes place, and the pigment settles at once free from any oil. The perfectly limpid solution of the oil is decanted, and successive small quantities of ether added to wash the precipitate free from the last traces of oil. This washing may, in the case of white-lead, be entirely conducted by decantation, as the lead pigment, owing to its great density, is more easily separated from the oil than any other pigment.

Even light flocculent pigments like oxide of zinc settle in a few seconds when fresh ether is used in such great excess, as it preserves great limpidness and allows of immediate settling. Some raw siennas and umbers are so fine that they take more time to settle, and may even require to be decanted through triple Swedish filter paper; but most pigments are obtained in such a flocculent condition that filtration is rapid and easy.

By using 100 c.c. of ether to every grm. of pigment the latter is absolutely freed from oil, and after three or four washings to clear it of mother-liquor, it may be transferred to a filter and weighed or dried in the flask after the last decantation. On dissolving the white-lead, or oxide of zinc, or other easily dissolved pigment, in cold dilute nitric acid after the above treatment, it will be found that a perfectly clear solution will be obtained, giving no trace of cloudiness, showing that no trace of oil or oleic acid adheres to the solid pigment.

On passing sulphuretted hydrogen through the ethereal solution of the oil, no trace of colouration is produced, showing that no oleate of lead or other lead compound has gone into solution with the oil, so that an absolute separation has taken place, as this test will show one part of dissolved lead in a million of pigment.

On distilling off the ether and heating to drive out any traces of alcohol, the oil is obtained pure and may be weighed.

I have conducted hundreds of analyses in this way, but will only quote some typical results of experiments which were done to test the process. The mixtures, when excess of oil was added to the commercial paint, were made most intimately by long grinding in a mortar.

Taken.		Found.	
White-lead.	Oil.	White-lead.	Oil.
88.48	11.52	88.51	11.56
91.75	8.25	91.64	8.37
93.50	6.50	93.46	6.51
Zinc oxide.	Oil.	Zinc oxide.	Oil.
81.73	18.27	81.75	18.18
77.44	22.56	77.62	22.60
Ultramarine.	Oil.	Ultramarine.	Oil.
73.79	26.21	73.74	26.25
78.22	21.78	78.23	21.80
Raw sienna.	Oil.	Raw sienna.	Oil.
83.21	16.79	83.25	16.74
79.43	20.57	79.43	20.62

Results Obtained with Mixtures of Butters and of various Fatty Matters by the Use of the New Method for Detecting the Falsification of Butters.—Auguste Houzeau.—The author observes the turbidity of melted and filtered samples. Those which are partially insoluble must be falsified. Those which are less turbid, like normal butters, may be pure.—*Compt. Rend.*, cxvi., No. 20.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

FIRST PAPER: THE ANALYSIS OF BARIC BROMIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 258).

Preparation of Materials.

Baric Bromide.—This substance was prepared in five distinct ways, with the intention of determining whether the salt is capable of being obtained in a perfectly typical state.

In the first place pure baric carbonate was prepared from pure baric nitrate. To make this latter substance the baric nitrate of commerce ("purissimum"), containing traces of strontium, calcium, potassium, and sodium, was re-crystallised seven times from boiling water by cooling. Baric nitrate is the most convenient starting point for the preparation of a typical barium salt, since its solubility rapidly diminishes with the temperature, and is so much less than that of the calcium and strontium salts. Even after the second re-crystallisation the alcoholic fractionally precipitated extract of a large amount of the mother liquor, which had been evaporated with excess of pure hydrochloric acid, showed no trace of calcium or strontium bands in the spectroscop. The pure salt, which had been re-crystallised seven times, was dissolved in a large platinum vessel in water which had been distilled in a platinum retort, and was treated with an excess of pure ammonia water which had also never come in contact with glass or porcelain. Into this perfectly clear solution was led a current of pure carbon dioxide, prepared by the action of pure sulphuric acid on sodic hydric carbonate. It was found impossible to free such carbonic acid from a trace of sodium, shown by conducting the gas into a lamp flame, as long as the sodic hydric carbonate was dry. After this last substance had been submerged under two inches of water, the gas evolved was easily obtained in a perfectly pure state by passing it through a sufficient number of washing bottles containing at first a weak solution of sodic hydric carbonate and finally pure water.

The pure baric carbonate was washed with hot distilled water until 25 c.c. of the wash water showed no trace of ammonia on the addition of Nessler's reagent. The last washing was with water which had been distilled in platinum. The snow-white preparation was dried and gently ignited over a spirit lamp in a platinum dish.

From this baric carbonate three different preparations of baric bromide were made, by dissolving it in two different samples of hydrobromic acid and varying other conditions. The first sample of acid was prepared from perfectly pure bromine. This had been made by the distillation of a mixture of potassic permanganate with a dilute solution of an excess of potassic bromide and pure sulphuric acid. Before being converted into hydrobromic acid the bromine was re-distilled after solution in potassic bromide and agitation with zincic oxide (Stas, *Mém. Acad. Belg.*, N. S., xliii., Part ii., p. 38). The bromine was in the first place poured into pure baric hydroxide, and, after the separation of the greater part of the baric bromide, was converted into hydrobromic acid by pure sulphuric acid. The baric hydroxide is easily freed from the usual trace of chlorine by five re-crystallisations from hot water; in this case the substance was crystallised nine times. The sulphuric acid had been re-distilled three times, the first and last portions being rejected.

The dilute hydrobromic acid, containing a small amount of free bromine set free by the remaining baric bromate, was distilled. The coloured first portion of the distillate was thrown away, and a portion of the second fraction was analysed to prove its purity. 1.82471 grms. (in

* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

vacuum) of silver (see "Silver"), dissolved with all possible care in the purest nitric acid, yielded 3.17641 grms. (in vacuum) of argentic bromide upon precipitation with a slight excess of the acid. Hence the percentage of silver in the precipitate must have been 57.446, a result which is essentially identical with Stas's result, 57.445.

In this hydrobromic acid a portion of the pure baric carbonate was dissolved, and the solution was evaporated with a slight excess of baric carbonate to the point of crystallisation. The crystals were dried over the water bath and ignited at a dull red heat over a Berzelius lamp for half an hour. The filtered solution was allowed to stand until neutral to phenolphthalein, showing that all the small amount of baric hydroxide formed upon heating had been eliminated, and after filtration was evaporated. As before, the mother liquor was rejected; the crystals were washed twice with pure re-distilled alcohol and dried in the air. These crystals formed the first preparation, designated I.a, and served for the two preliminary analyses.

The second preparation of baric bromide was made from a similar specimen of baric carbonate by its solution in hydrobromic acid, prepared essentially in the manner described in the work upon the atomic weight of copper (*Proc. Amer. Acad. A. and S.*, xxv., p. 197). To test the purity of this acid 1.60376 grms. (in vacuum) of silver were dissolved and precipitated by a slight excess of the acid, yielding 2.79184 grms. (in vacuum) of argentic bromide. Hence the percentage of silver in the precipitate was 57.444 (according to Stas 57.445). The baric bromide made from this acid was re-crystallised, ignited at dull redness, dissolved, allowed to stand exposed to the air, filtered, crystallised, dehydrated, and fused at bright redness by means of an alcohol lamp. Finally, after solution, filtration, slight acidification with hydrobromic acid, and two successive crystallisations, the small amount of substance which remained was used for Analyses 3 and 4 (Preparation No. I.b). The salt contained in the last mother liquor was fused into an absolutely clear limpid liquid, dissolved, faintly acidified, filtered, and re-crystallised, the crystals being washed with alcohol, and finally analysed under the designation No. I.c (Analysis 5). It is needless to say that in all the concluding operations platinum vessels and the purest water alone were used.

The second general method used in the preparation of baric bromide was based upon the decomposition of baric bromate. This salt was obtained in a very pure state by repeated re-crystallisation of the bromate remaining from the first preparation of hydrobromic acid by the method described above. In the course of the re-crystallisation it was noted that the glittering hard crystals emit brilliant flashes of bluish light upon being rubbed between the surfaces of moistened glass apparatus. This phenomenon takes place when there is no conceivable trace of organic matter present, and may be noticed even in the daylight. The substance was gradually raised to a dull red heat by means of a Berzelius lamp, no emission of light being noticed during its decomposition. The resultant baric bromide was dissolved, filtered, crystallised twice, washed with alcohol, and dried. After fusion over the spirit lamp the substance was re-dissolved, filtered, acidified with hydrobromic acid, and finally crystallised twice from water. Each yield of crystals was washed four times with the purest alcohol. In the first mother liquor a notable trace of sodium was found by the usual spectroscopic treatment, but no trace of calcium or strontium. The purest crystals were divided by yet another crystallisation into three fractions, which we may call II.a, II.b, and II.c. The last was obtained by the evaporation of all the mother liquor decanted from the first two.

The third method used for the preparation of baric bromide adopted baric nitrate as its starting point. This salt, which had been re-crystallised ten times, was dissolved in hot water and treated with the calculated amount of the purest obtainable potassium hydrate in a

platinum bottle. The resulting baric hydrate was re-crystallised ten times from hot water, without being removed from the bottle; but the spectroscope still showed noticeable traces of potassium upon the usual fractional treatment. The hydroxide was then precipitated three times successively from aqueous solution by means of pure alcohol, the precipitate being washed each time with alcohol, with the aid of the filter pump. Even the second mother liquor showed no trace of potassium to the most careful scrutiny.

The pure baric hydrate thus prepared was dissolved in pure water in the platinum bottle, boiled for some time to drive off the alcohol, transferred to a Bohemian flask, and saturated with pure bromine. This substance had been prepared as just described (see *ante*), with the additional treatment of solution in pure calcic bromide and several distillations. The mixture of baric bromide and bromate was evaporated, powdered, and gradually raised to fusion in a platinum vessel. The mass was grey before fusion and pale green afterwards. The greenish cake was dissolved in water, filtered, acidified, crystallised, dried, and fused; and then this same round of operations was again repeated. The last pure white cake of baric bromide was dissolved, the solution filtered, and after being very faintly acidified with hydrobromic acid, was again crystallised. The final crystals were washed four times with alcohol, and allowed to dry in the air. In the Table, which will appear later on, they are designated No. III. (Analyses 10, 11).

Since baric hydroxide is so easily re-crystallised it was hoped that a pure preparation might be obtained directly in this way from the baryta of commerce. It has been already said that five re-crystallisations remove the chlorine; five more remove the last traces of calcium. When, however, after seventeen re-crystallisations, the large amount of strontium present did not seem to be considerably diminished, this method was abandoned as a hopeless one.

A long series of qualitative and quantitative experiments upon the fractional precipitation of baric carbonate by the action of small amounts of carbon dioxide upon baryta water showed that this process also was utterly unfitted for the complete separation of strontium from barium, and accordingly this method was abandoned. The description and data of these experiments would require much room, and, since the work was not fruitful, they may well be omitted.

Because of all these unsatisfactory results, the baric hydrate was converted directly into baric bromide and bromate by the addition of pure bromine similar to that used in the preparation of Sample III. The large amount of bromide filtered off from the bromate was half crystallised out by boiling down the mother liquor in a platinum dish, treating with alcohol, and cooling. The mother liquor from these crystals contained most of the strontium. The solid was dissolved, boiled down, treated with alcohol, and cooled; and the new crystals were washed four times with alcohol. After repeating this round of operations once again, the mother liquor showed no trace of strontium.* The pure crystals yielded a faintly brownish mass upon fusion, and this in turn left a brownish precipitate upon solution. The clear filtered liquid was boiled down and treated with alcohol just as described above. The crystals were again fused, and again subjected to the same succession of operations. For the last time the crystals were raised to a dull red heat by means of a spirit lamp, and the residue was dissolved in the purest water in a platinum dish, allowed to stand exposed to the air until neutral, filtered, re-crystallised twice more, and washed with the purest alcohol. The resulting material was designated IV.a (Analyses 13, 14, 15). The last mother liquors were evaporated, and

* This method of freeing baric from strontic bromide suggests P. E. Browning's work with amyl alcohol, published since the experiment recorded above was completed (*Am. Journ. Sci.*, [3], xlv., 459).

yielded IV.b (Analysis 12). Only about 15 grms. of such pure material were obtained from a kilogram. of the baric hydroxide which served as the starting point. The earlier mother liquors containing strontium were used for the preparation of pure hydrobromic acid.

The fifth method for the preparation of baric bromide was the most complicated of all. A large amount of a solution of baric chloride ("purissimum") was allowed to stand for eighteen hours after the addition of a little pure baric hydrate and carbonate. To the filtered and slightly acidified liquid was added enough potassic chromate to precipitate about half the barium, the potassic chromate having been previously purified by continued shaking with a little baric chloride and hydrochloric acid, and by subsequent filtration. The large mass of baric chromate was washed by decantation with much water until no chlorine was to be found in the filtrate, and was almost wholly decomposed by strong nitric acid. The solution was diluted and shaken with the excess of baric chromate for a long time. Upon the neutralisation of the nitric acid in the clear yellow filtrate with pure sodic carbonate, the baric chromate was largely recovered, and after a thorough washing it was again dissolved in nitric acid, and the baric nitrate was repeatedly crystallised until it was wholly colourless and neutral. By means of gradually increasing heat, baric oxide was formed from this nitrate, the ignition taking place in a platinum crucible, and continuing until long after the frothing had ceased. The crucible itself lost several milligrams. during the process. The brownish residue was dissolved in water, and the clear colourless liquid was filtered from the brown precipitate. The baric hydroxide was neutralised with pure hydrobromic acid,* and the baric bromide was passed many times through the often repeated round of fusion, solution, filtration, and crystallisation, until the fused cake was perfectly clear and colourless. After being faintly acidified with hydrobromic acid, the pure salt was crystallised, washed, and dried as usual. This specimen, which had been growing smaller and smaller in amount during the manifold processes to which it had been subjected, was enough only for one analysis (No. 16) and was designated V.

Out of the baric bromate which remained from the fourth preparation two other specimens of baric bromide were prepared. The only point in which this preparation differed from the second method was the fact of the strong acidification of the bromide with hydrobromic acid just before the final series of crystallisations. The crystallisation was then continued until the mother-liquors proved to be absolutely neutral. The purest crystals were designated VI.a; the mother-liquor from them yielded VI.b (Analyses 17, 18, 19).

It seemed probable that if all these preparations gave about the same value for the molecular weight of baric bromide, they would fix this constant with comparative certainty. It is doubtful if the substance can be prepared in a state of absolute purity. Stas found it impossible to prepare any of his haloid salts in such a state (see Stas's "Untersuchungen," Aronstein, pp. 269, 279, 346), a small amount of silica always remaining. The attempt was made to eliminate the silica from the preparations described above by repeated ignition and fusion, and the exclusive use of platinum vessels; but it cannot be proved that the attempt was wholly successful. However, the salt was at least as pure as our usual standards of reference.

Silver.—Pure silver was prepared in the first place by the reduction of pure argentic chloride by pure milk sugar, after the well-known method recommended by Stas. A full description of the details is to be found in the account of the analysis of cupric bromide (*Proc. of the Amer. Acad. of Arts and Sciences*, xxv., 197, 198); indeed, some of the silver used in the present work was a portion of one of the large buttons made in 1890. Only

* This acid was from the same sample as that employed in making specimens I b and I.c.

in one particular was the mode of preparation modified: the silver was not heated with fused potassic hydroxide. Two or three buttons of the silver were fused with borax and sodic carbonate on hard-wood charcoal; this treatment made no essential change in its quantitative relations. The silver contained no oxygen, and gave very qualitative and quantitative evidence of purity (*Proc. of the Amer. Acad. of Arts and Sciences*, xxv., 197, 198; xxviii., 17, 28, 29).

All of the silver which has been thus far described was fused in the flame of ordinary illuminating gas. Since a strongly reducing flame was used, it was presumed that no silver sulphide was formed. Nevertheless, it was deemed advisable to prepare a sample of the metal which should be free from even the possibility of reproach. Ordinary hydrogen is apt to be quite as impure as illuminating gas, hence as little adapted for the present purpose. For this reason, pure hydrogen was made from pure hydrochloric acid by the action of zinc which was quite free from arsenic. The gas was driven through water, much potassic hydrate, through a tube containing beads moistened with argentic nitrate, and finally through potassic permanganate, into a gas-holder over water, where it remained for some time. It was burnt in an oxyhydrogen blowpipe provided with a complete platinum tip, and served for the fusion of the silver used in Experiment 19. For the support of the metal during its fusion a cupel of sugar charcoal had been made from pure sugar by the sole use of an alcohol lamp as the source of heat. The silver itself was made from the pure silver first described by dissolving it in nitric acid and electrolytically depositing it with the aid of two Bunsen cells (J. L. Hoskyns Abrahall, *Journ. Chem. Soc. Proc.*, 1892, p. 660), two plate of the same metal serving as electrodes. This method for the preparation of pure silver is a very satisfactory one. Since the silver was allowed to cool in an atmosphere of hydrogen, it could have contained no oxygen. The agreement of Experiment 19 with the others is satisfactory proof that the amount of sulphur contained in the first samples of silver must have been infinitesimal, if appreciable at all.

Other Materials.—The methods used for the preparation of pure water, pure nitric and sulphuric acids, and pure sodic carbonate, have been discussed at length in a previous paper (*Proc. of the Amer. Acad. of Arts and Sciences*, xxvi., 245—249). Precautions taken with regard to carbon dioxide, hydrobromic acid, and many other substances, are to be found under earlier heads. Alcohol was purified for the present investigation by repeated distillation in apparatus wholly free from cork or rubber connections. In some cases a platinum still was used.

The large mass of platinum used in the first experiments was kindly loaned by Professor Cooke, but subsequently a quantity was purchased especially for the work. The methods used in freeing the surface of these vessels from iron are described in the fourth paper upon the revision of the atomic weight of copper (*Proc. of the Amer. Acad. of Arts and Sciences*, xxvi., 249).

(To be continued.)

PROGRESS OF CHEMISTRY AS DEPICTED IN APPARATUS AND LABORATORIES.*

By H. CARRINGTON BOLTON.

FROM the very earliest times many arts were practised involving chemical operations, such as working in metals, purification of natural salts for pharmacy, &c., dyeing of cloths and the preparation of pigments, brewing of fermented liquors, &c.; hence we find that long before chemistry became a science, even before it became inocu-

* (Abstract). From the *Transactions of the New York Academy of Sciences*, Vol. XII.

lated with the virus of alchemy, furnaces and apparatus of earthenware, metal, and glass, adapted to special work, were in common use.

The important adjuncts to laboratory utensils for the mechanical operations of pulverising, grinding, sifting, &c., and the use of scales in a general way, date from the very beginnings of human industry; these we disregard in the main and confine our study to apparatus more strictly adapted to chemical operations.

In tracing the progress of chemistry by reviewing the forms and variety of apparatus used at different periods, we do not attempt to establish definitely the date of introduction of a given instrument except in a few instances to be noted in their places. To assign dates to the origin of apparatus that was universally employed before being specifically described is obviously impossible, especially since we shall depend upon drawings to illustrate the subject, and these drawings are commonly far more recent than the apparatus portrayed.

The Egyptians attained great skill in industrial arts at a remote period, and have left records of a most enduring character, pictures cut in their granite tombs and temples. There we see the processes of gold-washing and smelting; the use of blowpipes and of double bellows for intensifying heat, various forms of furnaces, and crucibles having a shape quite similar to those used to-day. Some of these crucibles preserved in the Berlin Museum date from the Fifteenth Century B.C.

Glass-blowing is a mechanical operation, but the preparation of the glass itself is a chemical process. The skill of the Egyptians in manufacturing glass is depicted on monuments of Thebes and Beni Hassan, and dates at least as far back as 2500 B.C.

Syphons for decanting wine, and on a large scale for draining land, were in use in the fifteenth century B.C. (Wilkinson).

The earliest chemical laboratories of which we have any knowledge are those that were connected with the Egyptian temples. Each temple had its library and its laboratory commonly situated in a definite part of the huge structure; at Edfoo the laboratory leads out of the Proseus-halls. In these laboratories the priests prepared the incense, oils, and other substances used in the temple services, and on the granite walls were carved the recipes and processes; these are still to be seen by the archaeologist.

The Israelites driven out of Egypt carried with them to the promised land knowledge of the technical and artistic skill of their contemporaries, and the Holy Bible contains frequent allusions to industrial arts. Cupellation is plainly described by Jeremiah, metallurgical operations by Job, Ezekiel, and others, and bellows by Jeremiah. This subject, however, I discussed in a paper read to the Academy April 12, 1892.

Geber, the Arabian physician and chemist of the Eighth Century, wrote very plainly of chemical processes, describing minutely solution, filtration, crystallisation, fusion, sublimation, distillation, cupellation, and various kinds of furnaces and apparatus employed in these operations. Geber's works first appeared in a Latin translation from the Arabic at Strassburg, 1529; since then many editions in modern languages have appeared, but the drawings in all those I have seen are obviously of comparatively recent date.

Geber describes in detail the aludel (or sublimatory of glass), the decensory, apparatus for filtration, and the water bath. This latter instrument, however, is said to have a more remote origin, having been invented by an alchemist named Mary, who is identified with Miriam the sister of Moses; and the French name *bain-marie* is advanced as proof of this claim.

Perhaps the earliest drawings of strictly chemical apparatus are those in the so-called manuscript of St. Mark, which is a Greek papyrus on the "sacred art," preserved in Venice and recently edited by Berthelot. This embraces among other treatises the *Chrysopoeia* of

Cleopatra, which dates from the beginning of the Eleventh Century. It contains, besides magical symbols, figures of distilling apparatus, the chief being an alembic with two beaks, resting on a furnace.

In manuscript No. 2327 of the Bibliothèque Nationale, Paris, which bears the date 1478, are interesting drawings of furnaces, alembics, matrasses, receivers, &c., of glass, earthenware, and metal. Some of them are copied from the manuscript of St. Mark. Professor Maspero, the Egyptian explorer, reports the discovery by natives of the subterranean laboratory of an alchemist of the Sixth or Seventh Century, at a point not far from Siout. This concealed laboratory contained a bronze furnace, the bronze door of another larger furnace, about fifty vases of bronze provided with beaks, some conical vessels resembling modern sand-baths, vases of alabaster, and gold foil of a low grade valued at over 350 dollars. In a corner of the dark chamber lay a heap of black fatty earth that the workmen seized upon and carried off, saying they would use it to transmute copper; "whiten" was their expression, but they evidenced a belief that this material was the "powder of projection" capable of changing copper to silver. This was in 1885. The substance on examination proved to be impregnated with some compound of arsenic, which would, of course, "whiten" copper.

The balance as an instrument of precision reached a high development under the Arabians as early as the Twelfth Century. The "Book of the Balance of Wisdom," written in the year 515 of the Hegira (1121—1122 A.D.) by al-Khazini describes minutely a water balance of great ingenuity, and the specific gravity determinations of solids and liquids made by its aid are marvellously accurate. The author also describes a specific gravity flask of a practical make which he calls the "conical instrument of Abu-r-Raihan." This treatise, with its illustrations of the balances and the flask, I analysed in a paper read to the Academy in 1876. (*Am. Chem.*, May, 1876).

In an interior view of a laboratory of the Fifteenth Century, by Vriese, very sumptuous appointments are seen; a lofty room with tiled floor, furnaces on the right under an overhanging hood, an altar on the left before which the alchemist prays on his knees, in the centre a table covered with apparatus, books, and musical instruments, in the foreground an alembic, overhead a lamp swinging from a ceiled roof. The whole indicates wealth and luxury contrasting strongly with later pictures of the laboratories of impoverished alchemists.

The interior of workshops of alchemists of the Sixteenth Century have been artistically painted by the celebrated Flemish artist David Teniers. Of these interiors I am acquainted with six different styles, having, however, many features in common.

The alchemists, influenced by the atmosphere of mystical associations prevailing in astrology and the black art, affected fanciful names for pieces of apparatus bearing accidental resemblance to objects in nature; the body of an alembic was a "cucurbit" or gourd; an alembic-head without a beak was a "blind alembic"; if the beak was joined to the body so as to make a circulatory apparatus, it was a "pelican," owing to its outline resembling to this bird; two alembics joined by beaks were "twins"; a flask with a very long neck was a "bolt-head"; a flask with its neck closed before the blowpipe was a "philosophic egg." Again the cucurbit surmounted by the alembic-head was symbolically called "homo galeatus," a man wearing a helmet.

(To be continued).

Use of Superphosphates. — Jules Joffre. — The author's experiments seem to show the possibility of the compounds of phosphoric acid soluble in water contained in manures being directly absorbed and assimilated by plants.—*Bull. de la Soc. Chim. de Paris*, ix.—x., No. 9.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, May 5th, 1893.

Dr. ARMSTRONG, President, in the Chair.

Hofmann Memorial Addresses.

THE PRESIDENT, in opening the proceedings, said they were met to do honour to the memory of a man to whom chemists throughout the world, and especially British chemists, are very deeply indebted—probably to a far greater extent than we shall ever be able to realise; a man who on account of his marvellous and manifold gifts will undoubtedly rank among the chemists of the Victorian era as second only to his great master Liebig. Hofmann, even if judged by his published work alone, would take the very highest position; but those who had known the man, however slightly, were aware that he was possessed of rare personal gifts which enabled him to exercise an influence extending far beyond the limits to which any purely scientific worker can attain. It is on this account very difficult to secure a satisfactory presentment of the man and especially of the influence which he directly and indirectly exercised on the development of chemical science and its industrial application. They, however, were fortunate in that they had succeeded in inducing several of the Fellows to co-operate in this arduous task, and although they could not hope to do all that is necessary, the contribution the Society was thus able to make will be exceptionally valuable, as the three gentlemen who would speak of Hofmann that night all had peculiar qualifications.

Lord Playfair, in days long ago, dwelt happily in the verdant and fertile fields of science, and the more often we had evidence of his perennial and vigorous youthfulness the more we must lament that he was ever led away into the tortuous paths of politics; in those almost prehistoric times he was not a mere spectator but an active worker, his name being associated in the records of science with those of the giants Bunsen and Joule. Among others there was a paper by him on "Transformations Produced by Catalytic Bodies," published forty-five years ago in the Society's memoirs, which was worthy of perusal even now, and which, he ventured to think, displayed greater philosophic grasp of the problem than the more recent essays on the subject. He had been astonished in reading through the early minutes of the Society to see how active an interest the then Dr. Lyon Playfair took in their work: how he was always proposing that something new should be done, and how very frequently his proposals were carried into effect. No one was so well qualified as Lord Playfair to picture to us the state of affairs chemical at the time of Hofmann's arrival here.

Sir Frederick Abel's qualifications were of a different order—he would speak directly of the man and of the conditions under which he worked at an especially interesting period in his career. He believed that Sir F. Abel's name was first on the list of Hofmann's first set of students, and that he was his first English assistant; he soon became and ever afterwards remained, he might say, his willing slave as well as friend, for Hofmann had the power—and hence his marvellous influence—of enslaving all who came under him, and of making them, whether they willed it or no, do the best work they were capable of. Sir Frederick Abel by virtue of his opportunities and his abilities was the man to whom alone we could look on the present occasion. His devotion to the Society was well known to most of the Fellows; but there were few besides the officers who have been concerned with him in the management of its affairs who are fully aware of the extent to which he had served the Society. His presence there to-night was in itself sufficient evidence of the deep interest he still took

in their work and of his willingness to sacrifice himself; as all knew, at the present time, he was engaged in the conduct of an enterprise of extreme difficulty and magnitude—more than sufficient to tax the powers of the majority of men, but which appeared in no way to satisfy his insatiable greed of work.

Of Dr. Perkin, who would speak of the outcome of a part of Hofmann's scientific work, it was needless to say much. He was a man of whom it could truly be said that his works are the measure of his worth. If the walls of the room in which they were assembled could speak, it would be of his labours before all others that they would have to tell. The story that he had to relate was of entrancing interest—a true tale of magic, but full of deepest moral.

Lord PLAYFAIR said that, although, when he was at Giessen, Hofmann was about two years his senior in age, Hofmann was studying mathematics and physics, and although he mixed with the active workers in Liebig's laboratory, he was not one of the body, and did not begin to work there until some time afterwards; it was originally intended that he should devote himself to philology and law, of which he was during some time a student. Referring to his remarkable linguistic powers, he said he had heard him make speeches in several languages, and especially remembered one occasion when, in 1867, at a memorable banquet given by the French chemists to those of foreign countries, Hofmann proposed the health of their hosts in a capital French speech.

He then spoke of the position of chemistry in England prior to Hofmann's arrival. Both in the last and the early part of the present century, England was not wanting in great chemical investigators. Among others, Lord Playfair referred to Dalton, incidentally mentioning that he could never forget seeing his venerable figure, supported on the arm of Dr. Joule, come daily to hear him lecture at Manchester on organic chemistry. Except Graham, under whom the speaker studied in Glasgow in 1835–36, following him to London as private laboratory assistant, no one, however, had thought of opening his laboratory to students. Graham's example, however, spread, and several colleges, and even the universities, slowly adopted the view that laboratories were necessary to teach and train the chemists of the future; but all who desired to study organic chemistry flocked to Giessen, and returning from there acted as missionaries in spreading a knowledge of the new organic chemistry. An extraordinary influence was exercised by the publication, in 1840, of Liebig's celebrated work, "Chemistry of Agriculture and Physiology," which was heightened by a triumphal tour, made two years later, by Liebig, through this country, in which he was personally conducted by the speaker. The immediate effect of Liebig's tour was to make chemistry a popular science, and to induce colleges to open laboratories, and hence it was that the Royal College of Chemistry was founded in 1845. Two wise men were mainly instrumental in its establishment—the Prince Consort and the Queen's physician, Sir James Clark. They saw that all the chemical laboratories in existence in this country were mere accessories or subordinate to professional training, the students entering them rarely wishing to become chemists; and they desired to found a college where chemistry might be studied for its own sake. A college of this kind without endowments could not have been created without a strong popular feeling had arisen, such as Liebig's work had promoted.

After referring to Hofmann's appointment, his remarkable lucidity, and his marvellous powers of exciting enthusiasm, Lord Playfair spoke of the early success of the College of Chemistry, and then proceeded to explain how it was that it so soon ceased to exist as an independent institution. Every landowner had thought that Liebig's book was to be his salvation, and when it was found not to produce the expected results, popular belief in chemistry declined, and the support accorded to the

college gradually dwindled. At this time the speaker resigned his professorship at the School of Mines, and Hofmann succeeded him, carrying with him the College of Chemistry, which then ceased to be an independent institution: the change was inevitable under the circumstances, but it was not good either for the college or chemical science. No doubt Hofmann felt this, and was affected by it when he was offered a professorship in the Berlin University, where he went in 1864.

Lord Playfair concluded his address by expressing the hope that he might live to see a new college or institute arise like a phoenix from the ashes of the old one, perhaps in connection with higher university teaching in London, as a supplement to, and not in competition with, existing laboratories, in which chemistry might be taught as an independent subject.

Sir FREDERICK ABEL, at the outset of his address, referred to the commencement of his own career as a chemist as an illustration of the difficulties attending the attempts of young beginners with limited resources to acquire a knowledge of practical and analytical chemistry, with a view of adopting the science as a profession, half a century ago. In the autumn of 1844, he had entered the laboratory of the Royal Polytechnic Institution, only to find that the sole means of acquiring some practical knowledge consisted in plodding unaided through Brande's Manual, endeavouring to acquire experimental skill by preparing the elements and their compounds according to the directions therein given, and to become acquainted with analysis by following Andrew Parnell's tables. Several other young chemists, who afterwards became prominent pupils of Hofmann, were in a similar position at that time, and so, when the temporary laboratories of the new college were opened in the autumn of 1845, there was a small band of aspirants impatiently waiting to avail themselves of the benefits of the system of instruction which had already acquired so high a reputation on the Continent.

Sir Frederick then recited the history of the efforts made in this country as early as 1843 to establish an institution where the systematic study of chemistry as a profession in itself could be pursued, referring to the prominent part taken in the matter by Dr. John Gardner, the translator of Liebig's *Letters on Chemistry*, and Mr. J. Lloyd Bullock, one of Liebig's earlier pupils, and pointing out how very nearly a National Practical School of Chemistry became associated with the Royal Institution. After the failure of the negotiations with the Royal Institution, the agitation was continued, and ultimately, at a public meeting at the temporary offices of the College of Chemistry on July 29, 1845, a definite form was given to the proposed Institution, and a Council and Executive Officers were appointed, after which the first all-important subject to receive anxious consideration was the appointment of a Professor. The circumstances attending Hofmann's appointment were next referred to.

Temporary laboratories were fitted up in George Street. Twenty-six students entered in the first session, among whom were F. A. Abel, C. L. Bloxam, Warren De la Rue, R. Galloway, Henry How, E. C. Nicholson, and Thomas Rowney.

Hofmann's complete sway over his pupils, said Sir F. Abel, was at once secured by his indomitable perseverance and inexhaustible patience with the dullest, his earnestness of manner, his clearness of exposition, rendered additionally attractive by an inherent quaintness and a power of happily rendering German expressions into graphic English. Those first two sessions of the College, in the scantily equipped laboratories, with make-shift contrivances of the crudest character and an utter absence of any convenience for conducting investigations, must have been a sore trial of patience and powers of endurance to the impetuous young teacher, and to the enthusiastic worker, whose only recreation was the pursuit of original research. When to these circumstances is added the

mental strain involved in the almost continuous pursuit of instruction and discussion in a foreign language, for at least eight hours daily, to say nothing of continued anxious consultations with the Council and officials of the College regarding ways and means; the heavy work connected with the erection and equipment of the permanent laboratories; the grappling with the problems of maintaining and fostering public interest in the Institution, and of keeping current expenses within very moderate bounds; it is self-evident that no small moral courage and powers of endurance were needed for the successful accomplishment of these duties; for the maintenance of the confident and apparently light-hearted demeanour, and of the power of instilling into others confidence of future success, which were peculiarly characteristic of Hofmann in those days of supreme difficulty. But these very characteristics, added to his genial and charming manner, high flow of spirits and originality in conversation and correspondence, secured to him devoted friends, not merely among colleagues and pupils, but in whichever direction social intercourse was opened up to him. Just as his earnestness of purpose and enthusiasm kindled corresponding qualities in a large proportion of his pupils, so also his sanguine temperament and airy treatment of difficulties maintained, among many of the early friends and important patrons of the struggling Institution, a steadfastness of purpose which otherwise would doubtless have speedily waned.

Hofmann's method of teaching and his powers as a lecturer were next alluded to.

Thirty-seven students entered in the second session, making sixty-three in all, and the laboratories became inconveniently crowded. The third session was commenced in the new laboratories in Oxford Street in October, 1846. These included a small private laboratory for the Professor, and here Hofmann at once resumed research work, Nicholson acting as his assistant.

There is but one opinion among those who can appreciate the stupendous difficulty of the task so brilliantly accomplished by Hofmann, in placing the College of Chemistry upon a sure foundation, and in securing to it, within a very few years, a high position among the chemical schools of Europe—that his success was ascribable to the possession of a happy and rare combination of the highest talents as a teacher with exceptional powers as an investigator, inexhaustible industry and energy, and an enthusiasm not to be subdued by any obstacles—a characteristic quality possessed in the highest degree by his great master, Liebig.

The severity of work and many-sided training which those who assisted Hofmann in the early days of the College of Chemistry was illustrated by an account of Sir F. Abel's experience during five years as an assistant.

Sir F. Abel then referred to the more prominent pupils of Hofmann; to the character of the researches carried on in the College; to Hofmann's faculty of gauging the abilities and special qualifications of those who worked under him, and his power of directing and stimulating them; to his marvellous literary and linguistic skill; and to the ease with which he made friends. The pleasure with which he always referred to his career in London was illustrated by a letter addressed by Hofmann to the Prince of Wales, who, as President of the Society of Arts, wrote to him, in 1882, congratulating him on being the recipient of the Albert medal.

Dr. PERKIN said that he was charged with the duty of giving an account of the rise and progress of the coal-tar colour industry, with which Hofmann's name was so inseparably connected, which he had been requested to make to a large extent autobiographical.

Aniline was Hofmann's first love, the subject of his first research, and he was the first to recognise the presence of benzene in coal-tar; in 1845, at his instigation, Charles Mansfield undertook the investigation of the coal-tar light oils, in the course of which he sacrificed

his life, while obtaining results of the utmost value, both scientifically and technically. Dr. Perkin said that he entered as a student under Hofmann when in his 15th year, at the time when the Royal College of Chemistry became a part of the School of Mines: he soon got through the ordinary analytical course, and began to work at research—the problem which he was set by Hofmann to solve being to prepare a base from the hydrocarbon anthracene. Although the desired base was not obtained, the compound now known as anthraquinone was prepared, and also chloro- and bromo-derivatives of anthracene, but the results of the analyses were unintelligible, and it never occurred to them to doubt the correctness of Dumas and Laurent's formula for anthracene, $C_{15}H_{12}$. The experience thus gained, however, proved of great value later on.

When in his 17th year, he was promoted to the position of an assistant in the Research Laboratory, and as he had necessarily little time for private work in the day time, a room at home was roughly fitted up where he was able to work in the evenings and during vacations. Here a research was carried on jointly with Mr. Church, also an assistant in the Research Laboratory at the College, on some colouring matters derived from dinitrobenzene and dinitronaphthalene, in the course of which amidoazonaphthalene was prepared, which appears to have been the first compound obtained of the diazo-class shown to possess dyeing powers.

At about this time the artificial formation of natural organic substances attracted much attention, and Hofmann specially referred to the importance of preparing quinine in his report of the Royal College of Chemistry, pointing out that, judging from its composition, it might be a derivative of naphthylamine. Dr. Perkin said that as a young chemist he was ambitious to work on the subject, and, probably fired by Hofmann's remarks, began to think how quinine might be formed: it occurred to him that it might be produced by oxidising allyltoluidine, and experiments in this direction were accordingly made—needless to say, to no purpose, but the results led him to experiment on the oxidation of salts of aniline, and on using potassium bichromate a product was obtained containing among other substances the colouring matter afterwards known as aniline purple, Tyrian purple, or mauve. These experiments were made at home in the Easter vacation of 1856. In the summer vacation the preparation of the colouring matter was undertaken on a small technical scale in the back garden at home, and ultimately the process was patented on August 26, 1856. Not long afterwards, in conjunction with his father and brother, he commenced the manufacture of the dye. The extraordinary difficulties to be overcome were then referred to; not only had all the mechanical appliances to be devised, but at this time benzene was made in but small quantities and nitric acid of sufficient strength could not be procured commercially; moreover, methods of dyeing with the new colour had to be worked out.

Dr. Perkin then referred to the discovery of fuchsine (rosaniline) in France, and explained how Messrs. Simpson, Maule, and Nicholson, original manufacturers of fine chemicals, began its manufacture. Through Nicholson, Hofmann at this time exercised an all-important influence on the industry. Hofmann had always insisted on the absolute necessity of obtaining products in as nearly pure a condition as possible, and had thoroughly imbued Nicholson, who had carried out several investigations under him, with this idea; owing to Nicholson's skill, his firm soon succeeded in supplying fuchsine in a crystallised condition, and the example thus set has been of the greatest value.

Hofmann's own early investigations of rosaniline and its various derivatives were then referred to, and, after sketching the further developments of the industry, Dr. Perkin drew attention to Hofmann's various researches bearing on derivatives of coal-tar products.

In the latter part of his address he more briefly referred to the rise of the alizarin industry, pointing out that,

although Hofmann had taken no part in this, it was undoubtedly the fact that his early introduction to anthracene, which he owed to Hofmann, was the cause of his becoming interested in the subject immediately Graebe and Liebermann's great discovery was announced. As in the case of the aniline colour industry, so in that of the alizarin industry, all the necessary machinery had to be devised, and many of the materials required had to be specially prepared for the purpose.

Hofmann's researches in connection with coal-tar colouring matters extended over a period of 25 years, from 1862 to 1887, and through these and the training which he imparted to those of his students who took part in the industry he exercised an influence unique in the history of modern industrial enterprise.

PHYSICAL SOCIETY.

Ordinary Meeting, May 20th, 1893.

Prof. A. W. RÜCKER, M.A., F.R.S., President, in the Chair.

MR. C. J. WOODWARD showed some "*Experiments with a Vibrating Bar.*"

On suspending the bar by two loops of cord, and placing it over a resonance box, the sound was greatly intensified. When placed crosswise, and partly over the box, a position could be found where no increase of sound resulted, whilst a little movement in either direction from this position caused a considerable increase.

The discussion on Dr. Lodge's paper, "*The Foundation of Dynamics,*" was then resumed.

Communications on the subject from Mr. S. H. Burbury, Dr. J. Johnstone Stoney, and Prof. E. F. Herroun were read.

Mr. BURBURY, referring to Dr. Lodge's deduction of conservation of energy on slip 6 of the paper, pointed out that two bodies may act on one another with equal and opposite forces and yet be moving with unequal velocities, and that the kinetic energy of such a system is not conserved. He did not see that denial of action at a distance was necessary to the proof given by the author.

Dr. STONEY said that only provisional and temporary foundations of dynamics could be deduced in the way followed by Dr. Lodge. It was necessary to first ascertain how the study of Nature is related to Ontology, but this essential, the author passed over by discarding metaphysics. When pursued in relation to the scientific study of Nature, Ontology throws a flood of light on most of the points dealt with in the paper.

Prof. HERROUN considered that universal contact action involves the conception of a homogeneous ether filling all space, and yet having ordinary matter dispersed through it; this he regarded as a metaphysical impossibility. If the medium be supposed molecular, then action at a distance was only postponed one step. He thought Mr. Heaviside was right in denying the objectivity of energy, for it had no more claim to be regarded as an entity than "life" or "death," "hardness" or "colour," or any other generalised abstraction.

Prof. MINCHIN said the first fundamental axiom of dynamics postulates the existence of *force* as an entity distinct from *matter*, *space*, and *time*, and this was the object of Newton's First Law. It also gave the criterion of the presence of force. To merely retain the law as defining *equal times* was to degrade it. As regards the supposed impossibility of defining uniform motion, he said, similar difficulties occur in all sciences, even in geometry. Nevertheless, a rational science of geometry existed. In dynamics we had notions of a right line and of uniform motion in it, although no criterion of either may exist. The fact that the science harmonises with ordinary experience constitutes its validity. In his opinion the extraordinary devices which had been suggested for

defining directions fixed in space were unnecessary, and merely served to cover the subject with ridicule.

He disagreed with Prof. Lodge in admitting the first law as a particular case of the second, for unless force was postulated (the function of the first law) the second became a mere definition, and not a law. Speaking of the third law, he said the author had made a serious error in stating that it could be deduced from the first, for the centre of mass of a system might be at rest without action and reaction necessarily being equal and opposite. The third law was not superfluous; neglecting it had led to great misconception and mystery about the principle of virtual work, and D'Alembert's principle, both of which are simple deductions from it.

In opposition to Dr. Lodge, he defended the ordinary definition of energy, and asserted that without the notion of *force* and *work*, the term *energy* loses all meaning.

Speaking of transference and transformation of energy, he inquired if the proof given could be applied to the case of a body sliding down a rough, rigid, inclined plane, for here the stress (friction) does work on the body but not on the plane, and there was no transference. He regretted that the expression "potential energy" was used in different senses in the paper, sometimes meaning "static energy," and at others "the available portion of the kinetic energy of a body."

Referring to the idea of all energy being ultimately kinetic, he asked if, by accepting this, the author meant to surrender the independent existence of force. If so, difficulties would arise; for example, in the kinetic theory of gases the expression for the pressure, $p = \frac{1}{3} \rho v^2$, was only arrived at by assuming the existence of force. The statement on the top of slip 9 about making a "moving body do work" was not necessarily true, as might be seen by considering the case of a sphere rolling down a rough inclined plane.

Prof. O. HENRICI thought axioms should be treated as true logical definitions, as for example in geometry. "Two straight lines cannot enclose a space." Every new notion required its axiom. In passing from geometry to kinematics, the idea of time presented itself, and the appropriate axiom was contained in Newton's first law. On approaching dynamics, force and mass were met with. He disagreed with Prof. Minchin in regarding force as most fundamental. Mass was more essential, for force might be abolished. On the other hand, he concurred with Prof. Minchin in thinking that the idea of a centre of mass was not axiomatic. Referring to Dr. Lodge's summary (*Nature*, May 18, 1893), he agreed with axiom (a) fully, and with (b) partially. Axiom 3 required further development. The critical point, however, was axiom 4: "Stress cannot exist in or across empty space." This he regarded as very incomplete, and maintained that axioms defining the properties of the ether were necessary to further progress. If varieties of space be contemplated, each advance required fresh axioms.

Dr. C. V. BURTON remarked that contact movement did not necessitate equal velocities; sliding motion was a case in point. Again, in deforming an incompressible fluid, although force and motion might exist, no work was done. Conservation could not be proved from denial of action at a distance. Speaking of the doctrine of transference and transformation of energy, he said it was a convenient working rule, but not true universally. Newton's laws were simple and consistent, but some doubt existed as to how much was definition and how much law, or fact.

Mr. Fournier d'Albe disagreed with Prof. Lodge in regarding the conception of uniform motion as a primary muscular sensation. It would be more correct to say that the conception was based on optical sensation, whilst the idea of force was derived from muscular sense. Newton's first law was not an axiom, for it could be proved experimentally. He thought Prof. Lodge's criterion of the identity of energy quite sufficient, if taken in conjunction with its conservation. The difference between the identity

of energy and of matter lay in the number of attributes by which they could be identified, energy having only one, viz., quantity.

Prof. AYRTON said the best foundations of dynamics depended on what was most easy to grasp. On this point great difference of opinion existed; some persons thought the idea of *force* more simple than those of *mass* or *time*, whilst others had contrary impressions. He could not admit that the conservation of energy could be deduced from denial of action at a distance. Experiments were necessary. In addition to the case previously mentioned of a body sliding on a plane, he thought a hard magnet acted on by a coil approaching it and conveying a current, was one in which Prof. Lodge's law of transference and transformation did not hold.

Mr. SWINBURNE protested against difference between theory and a working hypothesis being overlooked. All conceptions were based on experience, and ideas of ether and atoms derived from "jelly" and "cricket balls." We ought also to remember what "explanation" means, viz., describing the unfamiliar in terms of the more familiar. It was customary to describe the phenomena of fluids by reference to solids, because we were more familiar with solids; an intellectual fish would probably do the reverse. The so-called "theory of magnetism" which breaks up a bar of iron into a number of small pieces, each possessing the properties of the original bar, he regarded as absurd. It was no "explanation" and not a "theory." Ether might be used as a working hypothesis, but must not be treated as an entity.

Mr. BLAKESLEY questioned whether transference of energy was always accompanied by transformation, and he did not see why energy should be looked upon as—

$$(mv) \cdot \frac{v}{2},$$

in preference to any other subdivision of the factors. As regards effects being proportional to their causes, he pointed out that the heating of an electric circuit, and thermoelectric action, followed laws not linear.

Prof. S. P. THOMPSON, referring to the demonstration of the law of transference, &c., given on slip 8, said that attempts to translate it into Latin or Greek at once revealed the ambiguous character of the proof. Speaking of Ohm's law, he pointed out that R , a constant, was not an essential feature as Dr. Lodge supposed. Ohm never said R was constant.

In identifying energy, a difficulty presented itself, for one never came across it as a single thing, but as a product, and in being transformed the paths of the two factors might possibly be different.

Mr. DICKSON said the whole of geometry and dynamics could be based on verbal definitions. The conservation of energy could be written as—

$$\text{Kinetic energy} + \text{potential energy} = \text{a constant},$$

but on substituting the expressions for kinetic and potential energies, an identity resulted; therefore the original statement was not a law. Both the kinetic and potential energies of a system were functions of its configuration. Potential energy could not belong to a particle but to a system.

The PRESIDENT doubted whether Dr. Lodge's scheme was more simple, natural, and logical than the ordinary one. The statement in *Nature* (May 18th) that "strains were proportional to stresses" was simple enough, but it was questionable if "frequency of vibration is independent of amplitude" could be considered so. The author appeared to ignore *mass* in comparison with *force*, whereas the idea of *mass* seemed the more simple one. Referring to the identity of energy, he said that however far we trace it, we cannot identify its parts in molecular structure. He objected to carrying too far the ideas derived from matter in mass, to particles, and pointed out that by so doing the difficulty was only pushed one step further and not cleared up.

Dr. LODGE, in reply to Mr. Burbury, said two bodies never do attract one another; the thing which acted on either was the medium immediately in contact with it. Mr. Herroun had used metaphysical arguments against ether, but he (Prof. Lodge) thought it was a good thing to investigate ether. He agreed with what Prof. Minchin said about force and the first law of motion. Force was the more fundament, but mass was best as a standard unit. As regards ether, he was prepared to say that it has no motion. It possessed electromagnetic kinetic energy, and probably all the stress energy that exists. Referring to the slipping body mentioned by Prof. Minchin and Dr. Burton, he said that in speaking of the velocities of acting and reacting bodies being equal, he always meant that their velocities along the line of action were equal. The action between the sliding body and plane was a "catch and let go" one, like a fiddle bow and string. On the second law of thermodynamics he hoped to say something in a subsequent paper. When he spoke of R being constant as the essence of Ohm's law, he meant constancy as regards terms which appear in the equation—

$$\frac{E}{C} = R.$$

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, June 5, 1893.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—George Matthews Arnold, Charles Claude Carpenter, Frederick Henry Cheesewright, M.Inst.C.E., Ernest Prescott Hill, Henry Kemp, M.Inst.C.E., The Right Hon. Stuart Knill (Lord Mayor), Mrs. Lucas, Alexander Campbell Mackenzie, Mus. Doc., Carl Edward Melchers, Phineas Phillip, William Cuthbert Quilter, M.P., John Robbins, F.C.S., John Gorges Robinson, J.P., Thomas Thornton, and George White, B.A., LL.B.

The special thanks of the Members were returned for the following donations to the Fund for the Promotion of Experimental Research at Low Temperatures:—

Messrs. Crossley Bros.	£50
James Mansergh	£21
Sir Henry Doulton	£50
Captain A. Noble	£50

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

Microchemical Analysis of Rocks.—Frey (*Pharm. Schweiz. Wochenschrift*) treats the minerals with hydrofluosilicic acid, and examines the silicofluorides produced. If, e.g., a fragment of a sodiferous rock cemented with Canada balsam to a port-object is touched with a drop of pure hydrofluosilicic acid, there is formed sodium silicofluoride, which, on evaporation, leaves well-formed microscopic crystals of the hexagonal system, combinations of prisms, and pyramids. Potassiferous rocks yield small tesseral cubes, and calcium silicofluoride forms peculiar spindle-shaped tissues without plane boundary surfaces. In mixtures of silicates of these three elements there appear the different crystals in the exact proportion of the bases in the rock. Iron, manganese, and magnesium can be distinguished in a similar manner. These silicofluorides are certainly very similar, but if treated with chlorine the iron crystals turn yellow, those of manganese red, whilst those of magnesium remain colourless.

NOTICES OF BOOKS.

City and Guilds of London Institute for the Advancement of Technical Education. Report to the Governors.
April, 1893. Gresham College, Basinghall Street.

THIS report presents along with some very satisfactory features certain others which are less reassuring. On the one hand, it is pleasant to note that the number of day students has increased from 382 in the past Session to 412 in the current Session; that "the nature of the instruction both in the day and evening departments consists to a very large extent in practical work. Students spend the greater part of their time in the laboratories and workshops, and receive individual instruction and supervision."

It is satisfactory to find that some of the former students are now filling important positions in industrial establishments, and are capable of effecting real improvements. Even one such fact is a result of more importance than ten thousand successful examinations.

A less satisfactory feature is that the Corporation of London have withdrawn their financial support from the Institute. We are not disposed to believe that the Corporation has become indifferent to the importance of technical education, but the rumours of confiscation vented in different quarters have a necessarily restricting action upon munificence, whether private or corporate.

Another disappointing feature is the relatively small number of students who devote themselves to chemistry. At the Central Institution the numbers of students in chemistry for the Sessions 1890—91, 1891—92, and for the winter term of 1892, have been 12, 11, and 10; whilst the total of students in all four departments has been respectively 144, 160, and 172. Thus it will be at once seen that the number of chemistry students has declined not merely positively but relatively.

In the Finsbury Technical College the chemistry students have during the past three sessions increased from 37 to 41; small figures out of totals of 184, 198, and 213. An honour gained by this college is that Mr. H. D. Richmond, one of their former students, now Analyst to the Egyptian Government, is the discoverer of the new element masrium.

In the Evening Department chemistry comes out even worse. The number of students for the Session 1890—91 was 6 out of a total of 334, and that for 1891—92 7 out of 329! These figures are the more discouraging as the two Professors—H. E. Armstrong at the Central Institution, and R. Meldola at the Finsbury Technical College—are both decidedly "the right men in the right places."

Of course, it must be recognised that, as in all British educational institutions, examinations play far too prominent a part. The warnings of Mr. Auberon Herbert and his friends are as little noticed as those of Cassandra of old.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 20, May 15, 1893.

Determination of Boron.—Henri Moissan.—This paper will be inserted in full.

The Cultivation of the Soil and Nitrification.—P. P. Dehérain.—This paper also will be inserted at considerable length.

A Study of the Cadmium and Sal-ammoniac Battery.—A. Ditte.—Cadmium, in the cold, has no action on a solution of ammonium chloride, but its oxide may

combine with this chloride, yielding transparent crystals decomposable by water and containing $2(\text{NH}_4\text{Cl})\text{CdO}$. The electrolysis of a solution of sal-ammoniac under the electromotive action which ensues on the contact of a platinum-cadmium couple immersed in this liquid is still exothermic. In all the batteries examined the fundamental action is always an exothermic electrolysis of the saline solution yielding alkali and chlorine, which forms with the metal the corresponding chloride. The liquid is not homogeneous at all depths; it is more alkaline in its upper strata, and contains towards the bottom more cadmium (or zinc) chloride.

Influence of the Temperature of Re-Heating upon the Mechanical Properties and the Structure of Brass.—Georges Charpy.—The author proposes to study the modification of these properties as a function of the temperature of re-heating, and to examine if this phenomenon can be ascribed to an alteration of the structure of the alloy. His researches have hitherto been confined to a brass consisting of 67 parts of copper and 33 of zinc. It appears that in general brass is formed of two distinct alloys, the one crystalline and the other amorphous, playing the part of a cement. In the case of brass crystallisation improves the mechanical properties of the metal.

On Substituted Malic Acids.—Ph. A. Guye.—This paper may be regarded as an appendix to M. Colson's controversy with M. Friedel and M. Le Bel.

Action of Zinc Chloride upon Chloro-Camphor. Relation between Camphor and Carvacrol.—A. Etard. Carvol hydrochlorate behaves as a phenolic addition product, for it is split up by simple distillation (with or without zinc chloride) into carvacrol and HCl . Chloro-camphor behaves in the same manner as a carvacrol hydrochlorate. As a chemical function camphor may be regarded as a hydro-carvacrol.

A Certain Number of Organo-Metallic Compounds belonging to the Aromatic Series.—G. Perrier.—The compounds in question are aluminium chloride with ethers, with the acetone phenols, and with the phenols.

Inulase and the Indirect Alcoholic Fermentation of Inuline.—E. Bourquelot.—In many plants of the family of the Compositæ, especially in dahlias, the carbohydrate in reserve is not starch but inuline. Chemically these compounds differ by the circumstance that if treated by boiling dilute acids starch yields dextrose, whilst inuline produces levulose. From a physiological point of view they play the same part. It has long been known that the saccharification of starch is effected by a soluble ferment, diastase. It has been lately discovered by J. R. Green that the corresponding agent for inuline is inulase. Instead of using dilute sulphuric acid for converting inuline into a fermentible sugar the process may be effected by means of pure cultures of *Aspergillus niger*.

Contribution to the Study of the Chemical Phenomena of the Assimilation of Carbonic Acid by Chlorophyllaceous Plants.—A. Bach.—The author considers that the splitting up of hydrated carbonic acid, CO_3H_2 , follows a course analogous to the splitting up of sulphurous acid on exposure to solar radiation.

MEETINGS FOR THE WEEK.

TUESDAY, 13th.—Royal Medical and Chirurgical, 8.30.

Photographic, 8.

THURSDAY, 15th.—Royal, 4.30.

Chemical, 8, "Contributions to our Knowledge of the Aconite Alkaloids" (VI. Conversion of Aconitine into Isaconitine, by Prof. Dunstan and Mr. F. H. Carr; VII. Modifications of Aconitine Aurochloride, by Prof. Dunstan and Mr. H. A. D. Jowett. "Properties of Strong Solutions," and "Note on the Stereoisomerism of Nitrogen Compounds," by S. U. Pickering, F.R.S. And other papers.

FRIDAY, 16th.—Quekett Club, 8.

TO CORRESPONDENTS.

R. B.—In most cases ammonium acetate will answer as well as sodium acetate. When, however, continuous boiling is required, the sodium salt is preferred, as it does not decompose and lose acid so readily as the ammonium salt. We know no better book on the subject of Bread and Flour than the one by Jago.

FLETCHER'S THERMO-HYDROMETER.



IT is scarcely necessary to insist upon the vital importance of noting the temperature of a liquid when determining its specific gravity. Hitherto it has been necessary to employ separate instruments for the two observations, such combinations as were available being clumsy, slow, and untrustworthy. In FLETCHER'S THERMO-HYDROMETER the bulb of the Thermometer is BLOWN IN ONE PIECE WITH THE BULB OF THE HYDROMETER, and comes into direct contact with the liquid to be tested, thus ensuring the utmost sensitiveness. The Thermometer and Hydrometer scales being in juxtaposition on the same stem, A READING OF EACH CAN BE TAKEN SIMULTANEOUSLY.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1751.

FLAME SPECTRA AT HIGH TEMPERATURES.*

PART I. OXYHYDROGEN BLOWPIPE SPECTRA.

By W. N. HARTLEY, F.R.S.

BREWSTER, in 1842, first examined the spectra of salts with a flame of oxygen and coal-gas (*Proc. Roy. Soc. Edin.*, vi., p. 145).

Professor Norman Lockyer has given us maps of twenty-two metallic spectra at the temperature of the oxygen and coal-gas flame. The region observed lies between λ 7000 and 4000.

Preparatory to undertaking the study of spectroscopic phenomena connected with the Bessemer "blow" and the manufacture of steel generally, I have carefully observed the spectra of metals and metallic oxides obtained by submitting the substances to the oxyhydrogen flame.

Method of Investigation.—The method of obtaining spectra with flames at high temperatures is the following. Hydrogen proceeding from a large lead generator is burnt in a blowpipe with compressed oxygen. The blowpipe measures 3 in. in length by $\frac{3}{8}$ in. external diameter. The substances examined are supported in the flame on small plates of kyanite about 2 in. in length, $\frac{1}{20}$ in. in thickness, and $\frac{1}{4}$ in. in width. This mineral, which is found in masses in co. Donegal, contains 96 per cent of aluminium silicate, and is practically infusible. The spectra were all photographed with the instrument employed by me on former occasions for photographing ultra-violet spectra, illustrations of which were published in the *Chem. Soc. Journ.*, xli., p. 91, 1882. The dispersion of the instrument was that of one quartz prism of 60°.

Isochromatic plates developed with hydroquinone were largely used. Various dyes for sensitising and all kinds of developing substances were tried. The spectra were measured with an ivory scale divided into hundredths of an inch, and directly applied to the photographs, the division 20 on the scale being made to coincide with the yellow sodium line which appears in every photograph. It was found convenient to record the measurements on a gelatino-bromide paper print taken from an enlarged negative. Sometimes, for more careful and minute reference, it was found convenient to make an enlargement of the spectrum with the scale in position, but accurate measurements cannot be made in this way. It is necessary to use a low magnifying power and cross wires in the eye-piece.

For the identification of lines already known nothing more complicated is required, but to measure new lines and bands it was considered desirable to make use of a micrometer and microscope; the screw of the micrometer was cut with 100 threads to the inch, and the magnifying power generally used was 10 diameters.

Characters and Extent of the Spectra Observed.—Just as in the ordinary use of the spectroscope we must be prepared to see the lines of sodium, and in hydrocarbon flames the bands of carbon, so in these spectra the sodium lines and the strongest lines belonging to the emission spectrum of water vapour are also always present.

In addition, the kyanite yields the red line of lithium, which is no inconvenience, but a positive advantage, serving, as it does, to indicate where the spectra commence.

A large majority of the metals and their compounds all terminate somewhere about the strongest series of water

vapour lines. Typical non-metallic spectra are sulphur, selenium, and tellurium; the first yields a continuous spectrum with a series of beautiful fluted bands, the second a series of fine bands occurring at closer intervals, and the third is characterised by bands still closer together, and near the more refrangible termination of which four lines occurring in Hartley and Adeney's spark spectrum of tellurium are visible. Increase in atomic mass causes shorter periods of recurrence of bands. In line spectra it is the reverse; increase in atomic mass causes greater periods in the recurrence of lines. Charcoal and carbon monoxide yield chiefly continuous spectra; the latter, however, exhibits some carbon lines. The hydrocarbons yield the well-known spectrum of carbon bands with also those attributed to cyanogen. Of metallic elements, nickel, chromium, and cobalt yield purely line spectra; antimony, bismuth, silver, tin, lead, and gold beautiful banded spectra (spectra of the first order) accompanied by some few lines. These spectra are finer than those of selenium and tellurium.

Iron and copper exhibit lines and, less prominently, bands. Manganese has a beautiful series of bands and a group of three very closely adjacent lines. Aluminium gives a fine continuous spectrum with three lines, origin uncertain, zinc a continuous spectrum without lines, and cadmium a spectrum consisting of one single line only, λ 3260.2.

Of compounds, chromic trioxide yields a continuous spectrum with six lines belonging to the metal, copper oxide a fine band spectrum with two lines of the metal, magnesium sulphate gives a spectrum of magnesium oxide consisting of broad degraded bands composed of closely adjacent fine lines and one line belonging to the metal, λ 2852.

The sulphates of calcium, strontium, and barium give both bands of the oxides and lines of the elements. Phosphorus pentoxide yields a continuous spectrum with one peculiar line, seen also in the spectrum of arsenic.

The chlorides of the alkalis give also lines of the elements with a more or less continuous spectrum, which, it is believed, is due to the metal in each case. Lithium chloride gives no continuous spectrum.

The Volatility of Metals.—One of the most interesting facts ascertained by this investigation is the volatility of all the metals examined, except platinum, and particularly the extraordinary volatility of manganese, and, to some extent, of the infusible metal iridium. Metal believed to be pure iridium is seen to have diminished after the flame has played upon it for about two hours.

ATTEMPT AT A GENERAL METHOD OF CHEMICAL SYNTHESIS.

By RAOUL PICTET.

In order to develop from the totality of facts explained in my former papers a practical method of utilising low temperatures in chemical syntheses, it will be useful to recall the partial laws which we have already seen.

The fundamental hypothesis which has guided us and the experimental verifications have enabled us to establish eight laws:—

1. At very low temperatures, below -130° , no chemical reaction takes place, whatever substances are present.
2. All chemical reactions are manifested spontaneously at a certain temperature and under a certain pressure exerted upon the constituents; this is the temperature limit.
3. The same reactions may be obtained below the temperature limit if we apply auxiliary energy by the use of electric currents or discharges.
4. Exothermic reactions always present two phases: in the former we retain a control of the temperatures if we can remove from the combining bodies, by radiation, as

* Abstract of a Paper read before the Royal Society, June 1, 1893.

much heat as is produced at the same moment by the simultaneous effect of the affinities of the extraneous energies introduced into the substances. In the second phase, the temperature rises suddenly until the reaction takes place above the temperature limit.

The first phase is the reaction limit. The second phase is the reaction in mass.

5. Endothermic reactions are always limit reactions.

6. The dissociation of the products obtained by exothermic reactions corresponds to the laws of endothermic combinations and reciprocally.

7. The temperature limit of chemical reactions is not in a known simple relation with the apparent energy of the phenomenon. On the contrary, the quantities of heat liberated seem to class the ascending order of the temperature limit, especially in one and the same family of substances.

8. The electric spark and current seem to be the best media for supplying extraneous energy to limited chemical reactions.

With these eight partial laws we may establish a complete scientific programme for the discovery of a general method of chemical synthesis.

We begin by bringing in contact the simple bodies, and defining experimentally the laws which govern their combinations, the relations between their temperatures, the pressures, and the quantities of heat to be supplied in limited reactions.

As this first series of observations, must, on principle, give precise numerical values, we must never allow reactions in mass to interfere, as they disturb and modify the thermic conditions of the phenomenon. This condition, *sine qua non*, indicates at once the plan of operations to be followed. The chemist must have at command a powerful refrigeratory apparatus, by which he can at least reach temperatures of -130° to -150° , so as to paralyse all chemical reaction. Substances thus cooled are certainly below all the temperature limits.

The refrigerating tank must have a temperature which can be regulated at will from -130° to the ordinary temperature.

A powerful induction coil yields sparks which must be made to strike, by means of insulated conductors through the substances to be combined, in the refrigerated enclosure.

When the reaction commences, the heat produced each moment by the weight of the compounds obtained must be withdrawn by radiation, so that the temperature at which the reaction is produced may be kept constant.

The quantities of energy represented by the electric current in ampères and volts are equivalent to the endothermic phase of the reaction. The quantities of heat lost by radiation measure the exothermic phase.

The calorimetric measure effected in the refrigeratory enables us to know directly the effect of radiation for all the differences of temperature.

We shall on this principle constitute the first rational dynamic table in chemistry, by studying all the simple bodies, two by two, three by three, &c. By combining by the same methods, and with the same appliances, the binary bodies with the simple bodies, we obtain the second dynamic table. Next we pass to the ternary substances, &c.

The successive experiments will discover the laws which govern the phenomena, and will in so far facilitate the knowledge of the utilisation of the dynamic tables.

The line of the greatest chemical declination of all bodies will thus be determined experimentally.

Chemical reactions will be defined in a manner as precise and certain as the fall of a body on an inclined plane by a single track without ambiguity. We shall know beforehand, for any reaction which we may wish to produce, all the conditions to be fulfilled so as to obtain only a single effect, *e.g.*, the fixation of a new element upon a given primitive nucleus.

The track will be known and the result certain. Under

this form we see the possibility of forming rationally by direct synthesis all the substances in nature.

It is probable that along with the electric spark we may utilise other sources of auxiliary energy, *e.g.*, the collateral chemical reactions produced in the series of substances studied, and which will yield a known number of calories. The subject of this immense research is scarcely touched upon; we have confined ourselves to lay down its principal lines.

The present experimental results give a preliminary sanction to this programme.

In concluding the exposition of these general views on the phenomena of ponderable matter, we see that the same equations of motion may represent as a simple function of distances:—

1. All astronomy and the phenomena of gravitation, the distance of bodies which attract each other, passing from infinity to distances where the action of the ether manifests itself to modify the law of Newton.

2. All cohesion where the totality of the physical phenomena of changes of state linked to calorific phenomena where the distances of the attracting bodies pass from the limits of gravitation to the distance of bodies refrigerated to the absolute zero.

3. All chemistry, phenomena of motion, when the distance of the attracting bodies is smaller than that observed at the absolute zero.

The equations of the movement of matter permit us thus to reduce these three sciences to a single formula, the numerical terms of which are not yet known, but from which we may logically deduce every observable phenomenon.—*Comptes Rendus*, cxvi., p. 1057.

A NEW METHOD FOR DETERMINING THE FATTY MATTER OF MILK.

By LEO. LIEBERMANN and S. SZÉKELY.

MOST of the better-known methods of determining the fat of milk, if they do not depend on purely physical principles, use ether as a solvent. None of these methods can be perfectly accurate, since ether, in addition to milk-fat, takes up other substances. This observation is not quite new; it was pointed out some time ago by one of the present writers (*Pharm. Centralhalle*, 1885), and has been noticed elsewhere, but it has not been utilised for an exact determination of the fat of milk.

It appears from the following experiments that the errors thus occasioned are not quite insignificant:—

The fat of a milk was determined according to the well-known method of Adams. We took the precaution of previously saturating the specially prepared commercial slips of paper with acid sodium phosphate (for the more ready elimination of any resinous acids present), and extracting them with ether. The fat obtained from the milk was dried and again dissolved in ether, when it was found that on this second solution a certain portion was not taken up by the ether. We filtered the ethereal solution, carefully washed the filter with ether, and after the expulsion of the ether we weighed the residue again.

In the first weighing we obtained 3.65 per cent; in the second, though all loss was carefully avoided, only 3.35 per cent. The difference was therefore 0.25 per cent, which did not consist of fat.

In a second portion of the same milk we again determined the fat by the Adams' method, extracting, however, with petroleum ether instead of with ether. We obtained 3.40 per cent fat. We have thus a proof that the first extraction with ether did not give an accurate result. The second result, obtained by re-dissolving the dried milk-fat, was correct, since the difference was only 0.05 per cent.

The fat was also determined in the same milk by Soxhlet's areometric process and by Hoppe Seyler's

method; the former process gave 3.69 per cent and the latter 3.85 per cent.

In a second experiment we obtained, on extraction with ether (Adams), 3.96 per cent, and on extracting the milk previously desiccated with sand 4.07 per cent. In both cases, on again dissolving, we found a residue insoluble in ether, after the removal of which the quantity of fat obtained according to Adams was reduced from 3.96 to 3.86 per cent; whilst the portion treated by the other process fell from 4.07 to 3.95 per cent. The same milk on extraction with petroleum ether gave 3.78 per cent of fat.

It is remarkable that the fats extracted respectively with ether or petroleum ether often differ in their outward appearance. The residue from ether is, as a rule, yellowish; that from petroleum ether pure white and perfectly soluble in the solvents of the fatty matters.

We instituted an entire series of comparative experiments, from which it appears, without exception, that higher percentages are always obtained with ether than with petroleum ether. These differences are so considerable that they cannot be explained by an excess of matter extracted by the ether from the prepared paper or from the impurities of the gypsum or the sand. It is certainly for the greatest part derived from the milk itself. We have found that the paper prepared for the Adams method yielded to ether only 0.002 grm., whilst sand and gypsum gave off only 0.011 grm.

We have further made comparative experiments with the method proposed some time ago by one of us (Liebermann), and with the method as modified by Wolff.

We found in a milk:—

According to Adams, with ether	=3.91 p. c.
„ Liebermann	=4.12 „
With Wolff's modification	=3.97 „
Extraction with petroleum ether (Adams)	=3.77 „

In another milk:—

According to Adams, with ether	=5.55 p. c.
„ Liebermann	=5.32 „
Wolff's modification	=5.17 „
Adams, with petroleum ether	=5.07 „

Considering that the differences on using petroleum ether are not unimportant, amounting on the average to 0.17 per cent, but in some cases exceeding 0.4 per cent, we consider ether unfit for the accurate determination of milk-fat, and recommend in its place light petroleum ether.

At the same time we propose a new, convenient, and accurate method, a further development of that which one of us (Liebermann) published some time ago (*Zeit. Anal. Chemie*, xxii., 383, and xxiii., 476).

The New Method.

Fifty c.c. milk at the temperature of the room are put in a glass cylinder about 25 c.m. in height and about 4½ c.m. internal diameter; there are added 5 c.c. of potassalye at 1.27 specific gravity, closed with a well-fitting cork, and well shaken.

To this mixture are added 50 c.c. of a light petroleum ether, the specific gravity of which is about 0.663, the boiling-point 60°, and which evaporates on the water-bath without residue. The glass is stoppered, and again vigorously shaken so as to form an emulsion. To this emulsion are added 50 c.c. alcohol of about 95.8 to 96 per cent, and the liquid is again well shaken. After at most four or five minutes the petroleum ether separates at the top, and the separation may be regarded as complete. We shake again three or four times, each time for a quarter of a minute, allowing each time the ether to separate out.

The petroleum ether will now have taken up all the fat. We ascertained this point by shaking up eleven specimens a different number of times, the first once and the eleventh

eleven times. Already after the third and fourth shaking we have found quantities of fat which differ from each other only to an unimportant degree. After once shaking 3.535 per cent, after twice shaking 3.54 per cent, and the results which we obtained between the third and the eleventh shaking fluctuated only between 3.55 and 3.56 per cent.

Of the stratum of petroleum ether, 20 c.c. are drawn off with a pipette and introduced into a small tared capsule, the capacity of which is about 40 to 50 c.c., and the neck of which is higher than 1 c.m., with a diameter of 1½ to 2 c.m. These small flasks are convenient, because the liquid does not readily rise out of them, and yet the evaporation goes on with sufficient rapidity. But of course small tared beakers or ordinary flasks may be used.

The flask is set upon a water-bath at a moderate heat, the petroleum ether is evaporated entirely away, and the residue is dried at from 110° to 120°, for which an hour is generally sufficient; the weight found, if multiplied by 5, gives the quantity of fat in 100 c.c.

The quantities of fat obtained by the new method may be easily re-calculated by the aid of the specific gravity into percentages by weight, so as to admit of a comparison with the Adams method, in which the milk is weighed. We remark that on the Adams method the extraction with petroleum ether must last for at least 3 hours.

The results of the new method vary from those of the gravimetric method by 0.066 in a positive direction, and by 0.037 per cent in a negative direction. But these deviations, in our opinion, are not necessarily founded on sources of error in the method, but are chiefly due to the circumstance that in the gravimetric method the milk is weighed, whilst in the new method it is measured, and that the re-calculation may occasion errors.—*Zeitschrift f. Anal. Chemie*, xxxv., p. 168.

PROGRESS OF CHEMISTRY AS DEPICTED IN APPARATUS AND LABORATORIES.*

By H. CARRINGTON BOLTON.

(Concluded from p. 272).

A SPECIAL form of furnace much extolled for alchemical operations was an "athanor," deathless, because the fire could be maintained indefinitely. The residuum of any distillation was a "caput mortuum," death's head. A cone-shaped bag for filtering was early known as "Hippocrates' sleeve"; the operating of closing a flask by fusing the neck was applying the "seal of Hermes"; fusing of two metals was their "marriage." A still more extravagant nomenclature was applied to chemical substances themselves, but of these and of the characters employed to designate them I have already addressed the Academy (December 11, 1882, and March 12, 1883). A single example will suffice. Basil Valentine wrote: "The greater the quantity of the eagle opposed to the lion the shorter the combat; torment the lion until he is weary and desires death. Make as much of eagle until it weeps, collect the tears and the blood of the lion and mix them in the philosophical vase." That is to say: "Dissolve the substance and volatilize it."

In Iheronimus Brunschwick's *Liber de arte distillandi compositis* (1500) are many coarse woodcuts representing distillations conducted under different planetary aspects; also a noteworthy interior of a pharmacy of the fifteenth century, the apothecary's assistant busy with a pestle, gallipots on shelves, scales on a hook, and the licence and certificates of the master conspicuously displayed.

The remarkable and abundant illustrations of the

* (Abstract). From the *Transactions of the New York Academy of Sciences*, Vol. XII.

operations of mining, treatment of ores by washing and smelting, in George Agricola's *De re metallica* (1556), are too well known to need mention.

The *Alchymia* of Andreas Libau (or Libavius), published at Frankfort in 1595, is conspicuous for accuracy of description and systematic arrangement of topics. He treats in this work of the *Encheria*, or manual operations, and of the *Chymia*, or substances, in separate books. The former he divides into two sections, one dealing with laboratory apparatus, and one with the construction and management of furnaces. He describes and figures an ideal laboratory provided not only with every requisite for chemical experimentation, but also the means of entertaining visitors, including such luxuries as baths, enclosed corridors for exercise in inclement weather, and a well stocked wine-cellar. This work, sometimes called the "First Text-book of Chemistry," contains woodcuts of a great variety of alembics having peculiar forms for special uses; also a distilling apparatus fitted with an ingenious system of condensers for very volatile liquids. Besides the usual funnels for filtering Libavius describes the now neglected method of filtering by capillary fibres of wool or asbestos; a process which, however, was known as early as 400 B.C., as I have shown in a paper read to the Academy Oct. 13, 1879. Filtration was often styled "*destillatio per filtrum*," and the method just named was known as "*destillatio per lacinias*;" it is practically capillary syphoning.

Libavius' sumptuous plans were never realised, but towards the close of the seventeenth century the first public laboratory was opened at Altdorf (near Nuremberg) under Prof. John Moritz Hoffman. In the same year (1683), the first government laboratory was established by Karl XI. at Stockholm; of this the first director was Urban Hjärne.

A woodcut in a work published in 1570 depicts in a very interesting way all the steps in the manufacture of sugar, men chopping the cane, others grinding and pressing it, large cauldrons for boiling the juice, conical moulds in a frame, and the completed sugar-loafs.

Distilling apparatus in great variety is figured in the *Elixir vite* of the Italian author Donato d'Eremita, published in 1624. This pharmaceutical work contains nineteen full-page plates engraved with delicate skill.

In Kircher's *Mundus Subterraneus* (1665) are engraved numerous forms of furnaces and stillatories, largely copied from Donato d'Eremita's work.

J. J. Becher, in his account of a "Portable laboratory" (1719), exhibits on a single plate sixty-four different articles, including the following: Crucibles, muffles, cupels or tests, moulds for making cupels and for casting metals, mortars, mills for grinding, bellows, tongs, forceps, a tripod for supporting dishes, a rabbits-foot for brushing powders, a hand screen to protect the face from heat, various vessels of wood, copper, and iron, scales for weighing (three styles), retorts, phials, funnels, bladders, besides an apron, a towel, a linen jacket, an hour-glass, candles, and tobacco-pipes!

Straw-rings for supporting round-bottomed vessels are pictured in Lefevre's *Traité* (1669).

The interior of the University laboratory at Utrecht, under the direction of Johann Conrad Barchusen, Professor of Medicine and Chemistry, is neatly figured in his *Pyrosophia*, published 1698. In this, as in others of the period, the prominence given to furnaces reflects the importance attributed to operations by fire.

Physical instruments of chemical application were slower in developing; thermoscopes appeared early in the seventeenth century, and thermometers somewhat later.* Torricelli discovered the barometer in 1643, and Pascal tested its utility on the Puy-de-Dôme five years later.

* Geber remarks that "Fire is not a thing which can be measured, therefore it happens that error is often committed in it." He evidently felt the need of thermometers.

Otto de Guericke's air-pump and frictional electric machine, together with the interesting experiments conducted with the Magdeburg hemispheres, are handsomely depicted in his celebrated treatise *De vacuo spatio*, published in 1672. This air pump and the hemispheres are preserved in the Royal Library, Berlin. The Hon. Robert Boyle improved Guericke's air pump in 1659, and used it in laying the foundations of pneumatic chemistry, a field that from this time occupies our attention almost exclusively. Boyle's air pump and accessory apparatus are figured in plates accompanying the several editions of his works.

As is well known, the earlier chemists paid little or no attention to gases, though they were familiar with processes which generated them; perhaps the study of gases was retarded by lack of inventive skill in handling them. Dr. Beddoes, writing of Mayow, and reflecting on this point, uses the following language: "To be sensible of the merit of these contrivances of Mayow, we have only to recollect how difficult it must have appeared to confine, divide, remove from vessel to vessel, examine, and manage at pleasure fugitive, incoercible, and impalpable fluids like that which we breathe."

In 1672 Boyle obtained hydrogen gas by the action of acids on iron filings, and showed its combustibility, but seems to have made no attempt to collect and examine the gas.

The first scientific experiments in pneumatic chemistry were made by John Mayow, an Oxford physician, born in 1645 and died at the age of 34 years. In 1669 he published a work entitled *De sal-nitro et spiritu nitro-aëreo*, in which he figures his apparatus and describes his methods. To confine and study any gas, the air, for example, he inverted a cucurbit in a pan of water, used a syphon to establish the level of the water within and without, and introduced a shelf into the wider part of the cucurbit, from which he hung substances whose action he examined. He used a burning glass to ignite substances, camphor for example, placed in the cucurbit; he also introduced a mouse in a cage supported on a tripod under the cucurbit. He adopted an ingenious plan for transferring gases from one vessel to another, shown in the engraving that accompanies his rare treatises. Mayow failed to distinguish different gases, but was the pioneer in the method of manipulating them. Of his anticipating later theories of combustion we make mere mention, as our theme excludes theory.

Mayow's contrivances were somewhat improved by the eminent English botanist, Rev. Dr. Stephen Hales. In his "*Vegetable Statics*" (1727) he describes an attempt to analyse the air with many ingenious devices. Hales heated substances in a retort communicating by means of a syphon with a receiver consisting of a flask inverted in a vessel of water, the flask being supported by a cord from above. He heated nitre in this way, and especially noted the permanency of the air obtained, but failed to examine the properties of the air; and he failed to differentiate the several gases obtained by his methods.

Even before Hales, however, an obscure physician in France, Moitrel d'Elément, had invented improved methods of handling gases. In 1719 he published a little pamphlet containing lucid instructions for measuring and collecting gases; especially noteworthy is the separation of generator and receiver first suggested by him. The poor physician's skill was unnoticed by his contemporaries. In his old age a benevolent person took him to America, where he died unhonoured and unsung.

In 1757 Professor Joseph Black, of Scotland, determined the true characteristics of "fixed air," but seems to have made no important addition to the apparatus for studying gases.

In 1767 Mr. Peter Woulfe published a paper in the *Phil. Trans.* describing an improved apparatus for condensing vapours without loss, and applied it to hydrochloric acid, ammonia, nitric acid, and other

substances obtained by distillation. The apparatus still bears his name.

The prodigious advance made by Dr. Joseph Priestley in the manipulation of gases won for him the appellation "Father of Pneumatic Chemistry." His prime invention was the insertion of a shelf into the vessel containing water, and the perforation of this shelf so as to admit of the gases ascending into receivers standing thereupon. This pneumatic trough is not mentioned by Priestley in his first chemical paper, published in 1772, entitled "Directions for Impregnating Water with Fixed Air." In this tract the accompanying figures illustrate his method of collecting the gases. A bottle for generating the carbonic acid, to the mouth of which is attached a bladder, and this in turn communicates with an inverted jar by a flexible "leather pipe sewn with waxed thread" and having quills thrust in both ends to keep them open. This simple apparatus was the forerunner of the modern soda-water machines.

In the first edition of Vol. I. of Priestley's "Experiments and Observations on Different Kind of Air," published two years later than the little treatise above noticed, the author modestly says "my apparatus for experiments on air is in fact nothing more than the apparatus of Dr. Hales, Dr. Brownrigg, and Mr. Cavendish, diversified and made a little more simple." He then describes the pneumatic trough, both for water and for quicksilver, the method of pouring air upward under water, the process of generating gases by heating substances in a gunbarrel, by aid of a burning glass in thin phials filled with quicksilver, and the way to pass an electric spark through gases in a jar over water or over quicksilver. This introductory chapter clearly shows the greatest progress in the manipulation of gases, and the way in which Priestley energetically applied his skill by the discovery of nine gases is well known to every student.

After the disastrous riots in Birmingham, July, 1791, in which Priestley's house and laboratory were wholly destroyed by an angry mob, an inventory was taken of Priestley's laboratory as a basis for damages. This inventory has been preserved, and affords detailed knowledge of the material resources of the chemists of the period. It is divided into groups, philosophical instruments, electrical, optical, mathematical, and chemical apparatus, with a small stock of substances, the whole footing up to the value of £605. The imperfections of some of the apparatus used by Priestley are shown by the fact that he experimented from December, 1782, to May, 1713, on the direct conversion of water into air by distillation only without the intervention of any other substance, to discover after all that this astonishing result was due solely to leaks in the porous earthen retorts employed in the process. The retorts, as well as other articles, had been supplied gratis by Joseph Wedgwood; and Priestley, writing for more, desired to have them glazed within and without. (Scientific Correspondence of Priestley. New York, 1892.)

Scheele, the poor apothecary in a little village of remote Sweden, had to contend with obstacles sufficient to crush any but the bravest heart. With a few bottles, bladders, common dishes, and the simple appliances of a primitive pharmacy, this man of expedients accomplished wonders. Scheele's apparatus for generating oxygen was a simple retort, to the neck of which he tied a bladder. He was not acquainted with the pneumatic trough at the time of his chief discoveries. (Scheele's "Air and Fire." London, 1780.)

In 1796 James Watt, the English engineer, published an account of a simplified "Pneumatic Apparatus for Preparing Factitious Airs." In this is figured an "air-holder" made of tin-plate japanned inside and out, into which gas is conducted from the generating retort in a furnace, by means of a metallic tube bent at an angle of 45°, and terminating in the air-holder. Watt lays great

stress on the advantages of inclining the "lower pipe," as stated, though Hales certainly anticipated him in this point. This pneumatic apparatus was manufactured by Boulton and Watt, at Soho, in two forms; a large size sold for £10 2s. 6d., including auxiliary articles, and a portable apparatus for £3 15s. The pamphlet states that this apparatus are especially adapted for procuring "hydrocarbonate and oxygen air."

Meanwhile, across the Channel, in Paris, the opulent physicist and chemist, the unfortunate Lavoisier, enjoyed the advantages of highly specialised and admirably constructed apparatus of every description. An inspection of the plates in the *Traite élémentaire de chimie* (1798) shows what a wealth of excellent utensils he had at his command. Two sketches by the pencil of Mme. Lavoisier introduce us into his laboratory while he is conducting experiments in the respiration of a man at work and of a man in repose. After Lavoisier's legalised murder, an inventory of his laboratory was made by a government commission, among whom was the distinguished Nicholas Leblanc.

Accurate balances now became most important adjuncts to chemical laboratories.

Towards the close of the last century Italy contributed chemical research to two inventions of marvellous power—the Galvanic trough and the Voltaic pile, destined to electrify material human progress.

To sketch the development of chemical apparatus in this century would prolong this superficial review unnecessarily; modern appliances are distinguished by careful adaptation of the means to the end, and are improved by the introduction of coal-gas for heating purposes, by the use of india-rubber tubing and platinum vessels, and by the delicate products of the glass blowers' skill. To these features may be added novel contrivances for analytical chemistry, a field too recent to require elucidation.

(The paper was illustrated with 80 lantern views of the apparatus and laboratories described, including also exterior and interior views of the following institutions: Laboratories of the Museum in Paris, of Strasburg University, Bonn University, College of New Jersey, Kent Laboratory of Yale University, University of Michigan, Lehigh University, Cornell University, College of the City of New York, Women's Medical College of the New York Infirmary, and School of Mines, Columbia College.)

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

FIRST PAPER: THE ANALYSIS OF BARIC BROMIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 271).

The Method of Analysis.

Thus far it has been found possible to determine accurately only the ratio of baric bromide to silver and argentic bromide. Unfortunately no accurate method for the direct determination of the amount of metal present is known to exist; hence a complete analysis is impossible.

The usual scheme of operations was very simple. The baric bromide, after having been pulverised in an agate mortar, was heated for a long time at 200–400°; it was then gradually raised to dull redness, and maintained for some time at that temperature. Repeated heating sometimes caused a very slight loss, due to increased decomposition; but more usually the weight remained constant. The drying oven was a large porcelain crucible, and at first illuminating gas was used as the source of heat.

* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

Afterwards, when a faint trace of cloudiness found in the solution of the baric bromide was traced to the formation of baric sulphate from the sulphur in the illuminating gas, an alcohol lamp was used exclusively. In Analyses 3, 4, 15, 16, and 17, the amount of this insoluble residue was determined, and appropriate correction was made. In Analyses 6, 7, 9, and 12, the cloudiness of the solution was so slight as to be inessential, while in Analyses 2, 5, 8, 10, 11, 14, 18, and 19, the neutral solution of the baric bromide was absolutely clear.

The method of weighing was precisely similar to that employed with anhydrous cupric sulphate (*Proc. Amer. Acad. Arts and Sciences*, xxvi., 243, 252). Afterwards the salt was dissolved in the purest boiled water, and the traces of baric hydrate and carbonate present were determined in the manner which has been already described (see *ante*). The appropriate correction having been applied to the last weight of the baric bromide, the solution was diluted and transferred to a glass-stoppered Erlenmeyer flask. To this was added about the corresponding amount of accurately weighed silver, which had been dissolved in the purest nitric acid with all possible precautions (*Proc. Amer. Acad. Arts and Sciences*, xxv., 198). The argentic nitrate solution had been freed from the lower oxides of nitrogen by long heating at 100° in an inclined flask, and both solutions were quite cold at the moment of precipitation. Daylight was carefully excluded during this operation, as well as during the subsequent ones. After violent shaking, the precipitate was allowed to settle, and the excess of bromine or silver was determined by titration. It is well known that even here there is a slight difference between the end points, although the possible error is very much less than with the chloride. In the Table the mean between the two extremes is recorded; and in general the observations and method of treatment corresponded essentially with those since published for the late J. L. Hoskyns Abrahall in the account of his interesting work on the atomic weight of boron (edited by T. Ewan and P. J. Hartog, *Journ. Chem. Soc. Proc.*, 1892, p. 663), to which the reader is referred. The end point was always determined by titrating backward and forward until there could be no doubt of its accuracy, a c.c. of each of the solutions employed corresponding to one m.grm. of silver. In the final experiments the solutions were weighed as well as measured. For these experiments a dark room was built, and provided with an arrangement essentially similar to that described by Stas (Aronstein's translation, page 45) for condensing a beam of yellow light upon the surface of the liquid in the flask, leaving the precipitate in darkness.

In some cases the baric bromide was poured into the argentic nitrate (*e.g.*, Experiment 14, 15, 16), instead of *vice versa*. This difference of procedure seemed to increase the distance between the two end points, but not to influence the final averaged result (compare Stas, *Mém. Acad. Belg.*, xliii., Introduction).

In most cases a slight excess of hydrobromic acid was added before filtering, but the amount recorded in the Table always represents that which was equivalent to the end point of the reaction. In Experiments 3, 6, 12, 14, and 15, where argentic nitrate was added in excess before filtration, the total amount of silver given in the Table signifies the sum of the amount of silver weighed out and that which was added to attain the end point. The extra silver is, of course, not counted. The agreement of Analyses 14 and 15 with 18 and 19 is sufficient to show the accuracy of both methods. The clear yellow precipitate was washed by decantation until the filtrate became wholly neutral, and was collected and weighed on a Gooch crucible. The first filtrates were always passed through the crucible several times, for fear that a trace of asbestos might have been carried away. One of the absolutely clear filtrates containing a trace of hydrobromic acid gave no sign of a reaction for silver after evaporation to small bulk.

In a number of experiments modifications in the methods described above were introduced. The most important change was the one adopted in Analyses 2, 8, 14, and 18. In these four cases the baric bromide was not heated at all, but the crystallised salt was dissolved directly in water.* In order to determine the amount of anhydrous salt which must have been present in these specimens, parallel determinations of the water of crystallisation were made with the greatest care upon precisely similar samples. The agreement of these results with the others is the best possible proof of the accuracy of the alkalimetric correction applied to those determinations in which the substance had been ignited.

In Experiments 4 and 13 the baric bromide was fused. In Analyses 6, 14, 15, 18, and 19, the argentic bromide was fused, and the weight of the fused salt is recorded in the final Table. In the first case the substance had been slightly darkened by exposure to light; hence a little pure bromine vapour was added to the glass tube in which the fusion was conducted, and the bromide gained 0.07 m.grm. during the process. The other results are tabulated below.

No. of analysis.	Weight of argentic bromide before fusion.	Loss of argentic bromide on fusion.
	Grms.	Grm.
14	7.17411	0.00018
15	4.4583	0.00001
18	3.63751	0.00013
19	4.37867	0.00000

In Experiment 11 a hard glass tube with small rubber stoppers was employed for the ignition of the baric bromide, but it was attacked by the salt and gained 0.10 m.grm. during the heating. This gain corresponds to a loss of about the same weight of bromine, assuming all the barium which combined with the glass to have been converted to the oxide. For this reason the amount of hydrobromic acid recorded in the seventh column of the final Table is about 0.12 c.c. too large. In calculating the corrected weights of baric bromide, silver, and argentic bromide, allowance is made for all these facts. Because of the complication of all these little corrections, the glass tube was abandoned and the platinum crucible was again used.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 18th, 1893.

Dr. ARMSTRONG, President, in the Chair.

MR. H. A. D. JOWETT was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. S. W. M. Davy, Sharrow View, Sharrow, Sheffield; James John Howitt, Dunley, Toft Road, Knutsford; John Walter Leather, 15, Bradgate Road, Catford, S.E.; K. P. McElroy, 1412, Sixteenth Street, Washington, U.S.A.; John Watson Napier, Minto House, Edinburgh; Claude Theodore James Vautin, 10, Hanover Square, London; Edward Augustus Warmington, 266, Castle Street, Dudley.

Of the following papers those marked * were read:—

*20. "Studies on the Formation of Ozone." (II.) By W. A. SHENSTONE and MARTIN PRIEST.

The authors have submitted a known volume of oxygen confined in an ozone generator of the Brodie pattern to

* This procedure was suggested by a part of Marignac's work on the chloride (*loc. cit.*).

the influence of discharges produced by varying differences of potential, and have determined the amount of ozone produced by observing the change in volume by means of a mercury manometer. A full description is given of the contact breaker used, of the means adopted to measure the differences of potential, to prevent the ozone coming into contact with the mercury, &c.; in some of the experiments the discharge from an induction coil, in others that from an influence machine, was used. The following conclusions are drawn:—

1. It is possible to obtain very fairly concordant results.

2. Provided that the path of the discharge be not too short at any point in the generator, the maximum proportion of ozone that can be produced at a given temperature and pressure is nearly independent of the difference of potential employed, provided that this be between the limits of 33 and 69 C.G.S. (electrostatic) units.

3. If the path of the discharge be very short at any point in the generator, the maximum proportion of ozone that can be obtained has an inverse relation to the difference of potential employed.

4. The rapidity with which oxygen is converted into ozone in a given ozone generator, and under given conditions of temperature and pressure, is greater when great than when small differences of potential are employed, or, in other words, a given percentage of ozone can be obtained more quickly by employing a high difference of potential than by means of a lower one.

5. The maximum proportion of ozone that is obtained in a given generator, at given temperature and pressure, is less when the number of discharges in unit of time is very great than when it is more moderate.

6. The highest proportions of ozone can be obtained (at given temperature and pressure, and if a given difference of potential be employed) by using a generator made of very thin glass and in which the inner tube fits into the outer tube rather closely, but such a generator acts very slowly if the mingling of its contents depend upon diffusion.

7. A greater proportion of oxygen can be converted into ozone in a given generator by means of a given difference of potential, the gas being maintained at a given temperature and pressure, by the action of an induction coil than by means of a "Wimshurst" or "Voss" machine.

The authors conclude from their results that the silent discharge acts by decomposing oxygen molecules into their atoms, which subsequently re-combine to a greater or less extent (according to the temperature and pressure) to form the triatomic molecules of ozone; and that ozone is not formed by the direct action of the discharge.

DISCUSSION.

Professor McLEOD referred to the heating effect of the discharge, and asked whether it had been noticed that a rise of temperature took place in the inner vessel of the generator which might account for the decomposition. He drew attention to the possibility of producing ozone in considerable quantity by subjecting oxygen under pressure to the influence of the discharge in a tube one end of which was at a low temperature: unfortunately the tendency of ozone to explode when in the liquid condition appeared to be a barrier to the successful application of this method.

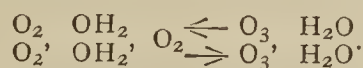
Professor RAMSAY commented on the fact that the authors had paid attention only to the influence of difference of potential, and had not taken into account what was probably of more importance, viz., the quantity of electricity in the discharge.

Mr. CROOKES concurred in Professor Ramsay's criticism, and said that perhaps the difference observed in the case of the coil and influence machine might be ascribable to this, as the coil would afford a larger quantity of electricity; and that a rapid discharge would also afford a smaller quantity of electricity than a slow one. Locally the temperature might be very high in such tubes. He

then referred to the difficulty he had frequently met with in causing a discharge to pass in "Tesla" tubes: a tube through which no discharge would pass during several minutes would suddenly become luminous, but only when charged dangerously near to the breaking point.

Mr. G. N. HUNTLEY asked whether Mr. Shenstone intended to study the effect of temperature on the yield of ozone; as it was a substance in the formation of which heat was absorbed, its stability should reach a maximum at a temperature fixed by its physical constants, and either above or below this temperature the yield of ozone should fall off. In connection with this, the production of ozone at 1200—1300° C., observed by Troost and Hautefeuille, required confirmation.

The PRESIDENT regretted that no electricians were present to discuss the arrangements adopted by the authors. Professor J. J. Thomson, he knew, held the view that the electric discharge in gases was of the nature of chemical action. Personally he was not satisfied with the evidence adduced by Cundall and Shenstone that only oxygen was concerned in the production of ozone; he was of opinion that it would eventually have to be admitted that the formation of ozone was the outcome of an electrolytic change, in which probably conducting moisture was concerned, somewhat as expressed by the symbols—



Mr. SHENSTONE, in reply, said that the electricity does not flow directly from the induction coil, or machine, into the ozone generator. It acts inductively; the ozone generator being a sort of condenser with a compound dielectric consisting of two layers of glass with a layer of oxygen between them. The discharge inside the ozone generator depends on a surface electrification set up on the glass. The "quantity" of electricity which passes through the oxygen in a given ozone generator at each discharge depends on the difference of potential thus set up, and this in its turn depends on the difference of potential of the inducing charge at the two electrodes of the generator. Therefore when the difference of potential of the inducing charge is increased, the quantity of electricity which takes part in a discharge is increased, and *vice versa*, and we are in fact studying the effect of different "quantities" of electricity on the gas, and we know when we increase or decrease the quantity.

With regard to the suggestion that the greater "quantity" of the current of a coil may explain some of the phenomena, it would seem that this is not likely to influence the inductive effect of a charge at a given difference of potential. It would simply make it possible to bring up the discharge to the desired difference of potential somewhat more quickly by means of a coil than by means of a machine.

They had not observed any extra heating of the acid in the inner tube of the generator, but rather the contrary. Referring to Mr. Crookes's remarks, he said that they had sometimes observed that the production of ozone did not set in until after some time.

*21. "The Relative Strengths or 'Avidities' of some Compounds of Weak Acid Character." By JOHN SHIELDS, D.Sc., Ph.D.

The author has calculated the relative strengths of a number of compounds of weak acid character from the rate at which salt solutions hydrolyse ethylic acetate (*Phil. Mag.*, [5], xxxv., 365).

The comparison has been made in decinormal solution, the "dissociation ratio" being taken as the measure of relative strength or "avidity," and in order to obtain a better idea of their relative strengths the compounds examined have been compared with some of the stronger acids taken from Ostwald's tables. The results are contained in the following table, from which it will be seen that in decinormal solution, hydrogen chloride, for example, is about 100,000 times stronger than phenol.

Hydrogen chloride	100
Trichloroacetic acid	68
Dichloroacetic	33
Monochloroacetic acid.. .. .	4.3
Acetic	0.35
Biboric	0.0057
Hydrogen cyanide	0.0026
Phenol	0.00094
Carbonic acid	0.00091

*22. "The Boiling Points of Homologous Compounds. Part I. Simple and Mixed Ethers." By JAMES WALKER, Ph.D., D.Sc.

The author finds that the boiling points of many homologous series may be expressed by means of the relation $T = aM^b$, where T is the boiling point on the absolute scale, M the molecular weight, and a and b constants which have values peculiar to each series. He applies the formula to the ethers prepared and investigated by Dobriner (*Annalen*, ccxliii., 1) and Pinette (*Annalen*, ccxliii., 33). The difference between the calculated and observed values is generally considered less than a degree. The following rule is a deduction from the formula:—The logarithm of the ratio of the absolute boiling points of any two members of a homologous series, divided by the logarithm of the ratio of their molecular weights, is constant.

23. "The Conditions Determinative of Chemical Change." By HENRY E. ARMSTRONG.

Notwithstanding the large amount of evidence now placed on record that substances commonly supposed to be capable of directly interacting do so only in the presence of at least one other substance, chemists do not appear to have arrived at any clear and consistent understanding of the conditions determinative of chemical change: as each fresh case is recorded, we continue to express surprise, overlooking the fact that Faraday, in his early "Experimental Researches in Electricity," clearly foresaw what the conditions were, and that but a slight extension of his generalisations is needed to frame a comprehensive theory. The subject is of such importance that it appears to me desirable to discuss the bearing of recent observations, especially as they to some extent necessitate the modification of views that I have expressed elsewhere, and in order to attract the attention of physicists, to whom we must now look for guidance in these matters.

Eight years ago, in the course of the discussion on Mr. H. B. Baker's communication on "Combustion in Dried Gases" (*Proc. Chem. Soc.*, 1885, 40), I defined chemical action as *reversed electrolysis*: in other words, in order that chemical action may take place, it is essential that the system operated on comprise an electrolyte. I then pointed out that as neither hydrogen nor oxygen was an electrolyte, a mixture of only these two gases should not be explosive; and, moreover, that as water was not an electrolyte, and it was scarcely probable that water and oxygen or hydrogen would form an electrolyte, it was difficult to understand how the presence of water pure and simple should be of influence in the case of a mixture of hydrogen and oxygen. This forecast has since been verified, the remarkable series of experiments carried out by V. Meyer in conjunction with Krause and Askenasy having clearly demonstrated that the formation of water from hydrogen and oxygen takes place at an irregular rate, and is, therefore, dependent on the presence of a something other than water—I imagine an acid impurity. But this is a consideration which has not yet received the proper attention, and it is, therefore, desirable to emphasise its importance by reference to other cases. Mr. Baker's recent preliminary note on the influence of moisture in promoting chemical action (*Proc. Chem. Soc.*, p. 229) affords several interesting examples:—Thus, he states that neither does hydrogen chloride combine with ammonia nor is nitric oxide oxidised by oxygen if moisture

be excluded. In the former case, the addition of water should suffice to determine the combination, as water and hydrogen chloride together form a "composite electrolyte" (*cf. Roy. Soc. Proc.*, 1886, No. 243, p. 268); as neither nitric oxide nor oxygen, however, forms a composite electrolyte with water, in this case water alone should not determine the occurrence of change; but if by the introduction of a trace of "impurity" in addition to water the presence of a composite electrolyte were secured (however high its resistance, owing to the smallness of the amount of "impurity"), action would set in, and when once commenced would proceed at an increasing rate, as nitric acid would be formed and the resistance of the electrolyte would consequently diminish. On this account it will be a task of exceeding difficulty to experimentally demonstrate that nitric oxide and oxygen are inactive in presence of water alone; but there can be no doubt that such must eventually be admitted to be the case, provided always that it is permissible to extrapolate Kohlrausch's observations and to conclude from them that *pure* water is a dielectric. The gradual increase in the rate of change here contemplated corresponds to the period of induction observed by Bunsen and Roscoe in their observations on the interaction of chlorine and hydrogen; the statement recently made by Bodenstein and V. Meyer (*Berichte*, 1893, 1146) that a mixture of chlorine and hydrogen behaves irregularly on exposure to light is a valuable confirmation of Pringsheim's observations, and there is now no room for doubt that *pure* chlorine and hydrogen would be incapable of interacting. That no such irregularity is observed on heating iodine with hydrogen is not surprising, as hydrogen iodide would be formed from the very outset and the electrolyte present would exert a minimum resistance almost at once. There is, however, a significant difference in the behaviour of the two mixtures, as hydrogen chloride should behave as hydrogen iodide, so that the problem is but incompletely solved: it may be that the one mixture was more nearly pure than the other, or it may be that the formation of hydrogen chloride from hydrogen and chlorine, under the influence of light, is dependent on the presence of some particular substance, together with water, and does not take place under the influence of any substance capable of forming a composite electrolyte with water; probably, however, the difference observed is chiefly due to the fact that only one of the actions is reversible under the conditions prevailing in the experiments.

Lastly, attention may be directed to the formation of sulphuric oxide from sulphurous oxide and oxygen, which is readily effected in presence of a catalyst, such as finely divided platinum; it cannot be supposed that the mere presence of platinum would condition the occurrence of change, and doubtless moisture is also necessary, the platinum or other catalyst but serving to promote the oxidation of the sulphurous oxide at a temperature considerably below that at which sulphuric oxide decomposes when heated. The action of surfaces generally may well be of this character, and the converse influence they so frequently exercise is probably an effect of the same order.

I have elsewhere raised the question whether there may not be a difference between actions taking place under the influence of low and of high electromotive forces—whether water, *per se*, may not be an electrolyte towards high, though not towards low, forces in the case of high temperature changes, or those brought about under the influence of the electric spark, for example. More attentive consideration of the subject has led me to think that this is not the case, and that we must treat high temperature changes such as occur and are involved in gaseous explosions in the same way as those occurring under ordinary conditions and at low temperatures. From this point of view, Mr. Baker's statement that ammonia and hydrogen chloride do not combine is of extreme importance; the formation of ammonium chloride from these two compounds apparently involves no interchange,

but a mere combination of two substances each endowed with considerable "residual affinity," and there is no reason why a distinction should be drawn between such a case and that afforded by, say, *atoms of hydrogen and oxygen*, the difference being, it would seem, one of degree only: in fact, I am no longer inclined to believe that atoms are capable of directly uniting. In all cases at least one function of the (composite) electrolyte would appear to be that of providing the necessary "mechanism" whereby the degradation or discharge of the energy is effected. If this argument be sound, its logical extension involves the conclusion that *pure* gases should be dielectrics, *i.e.*, that the passage of an electric discharge through a gas like that of an explosive wave through, say, a mixture of hydrogen and oxygen, can only take place if an electrolyte be present. Hitherto but little attention has been paid to the electric discharge in gases which have been highly purified. The peculiar behaviour of Tesla tubes referred to by Mr. Crookes in the discussion on Mr. Shenstone's paper on the formation of ozone is, perhaps, explicable from this point of view—it may be that the atmosphere within the tube does not become conducting until sufficient moisture and "impurity" have been projected from its sides. It is conceivable that a similar explanation may hold good in the case of Professor Schuster's observation, that it is possible to urge a current of low electromotive force across a gas subjected to a high electromotive force in itself insufficient to cause a discharge in the gas; the atomic dissociation hypothesis put forward in explanation of the phenomenon does not appear to me to be sufficient.

Finally, the question arises, Can no line be drawn; are no two pure substances capable of combining or interacting:—For example, water and sulphuric anhydride? There is little to guide us here, but it seems not unlikely that water has special properties which enable it to act directly; moreover—perhaps because—in such cases composite electrolytes would result. Ammonium chloride, so long as it remains solid, is clearly a compound of a different order, and it may well be that compounds of this type are in no case directly obtainable from their constituents, because, under the conditions under which they are formed, they cannot behave as electrolytes.

Apparently, in all cases in which the molecular aggregates are formed—as in the case of solutions—we are dealing with dissociable and dissociating systems, and it is not improbable that we may ultimately find an explanation of the mechanism of such changes in this fact.

At present there is no information forthcoming whether simple electrolytes, such as fused silver chloride, for example, will condition chemical change in the way that water does—whether, for instance, silver chloride will condition the formation of hydrogen chloride from chlorine and hydrogen, so that a gas battery might be constructed of these three substances.

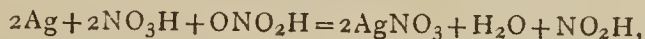
24. "The Nature of Depolarisers." By HENRY E. ARMSTRONG.

When an electric current is passed between plates of platinum through a solution of sulphuric acid, the hydrogen and oxygen are partly retained at the surfaces—and apparently also within the plates—and under these conditions are capable of interacting, as in the well-known Grove gas battery; so that in so far as the "gases" thus circumstanced are concerned the change may be expressed by a reversible equation. This reversal constitutes the well-known phenomenon termed polarisation by physicists.

Reversal owing to the retention of hydrogen in circuit is promoted to different extents by different metals—hence apparently the varying electromotive forces of single fluid cells containing different negative plates; and when the pressure is sufficient to retain the whole of the hydrogen at the plate, it becomes total—hence it is, for example, that zinc does not dissolve in sulphuric acid under great pressure.

Various substances known generally as depolarisers are used to prevent the accumulation of products of electrolysis and the consequent reversal of the action—such as copper sulphate in the case of the Daniell cell, and "nitric acid" in the case of the Grove and Bunsen cells; but whereas the action of copper sulphate is easy to understand, that of "nitric acid" offers many difficulties. As the heat of dissolution of copper in dilute sulphuric acid is a negative value (about 12,000 units), the displacement of copper by hydrogen, *i.e.*, the heat of dissolution of hydrogen in copper sulphate—is a positive value, so that not only does the presence of the copper sulphate prevent the accumulation of hydrogen, but in removing hydrogen it also serves to increase the electromotive force of the cell from about 37/46ths to about 50/46ths of a volt. The principle underlying this is extensible, even to cases in which one part of the cumulative effect of the cycle of change is a negative value. Thus, although copper has a negative heat of dissolution, it will readily dissolve in dilute sulphuric acid if it be used in place of zinc in a Grove cell, the negative heat of dissolution of copper being more than compensated for by the positive heat of dissolution of hydrogen in "nitric acid"; and it is well known that copper dissolves in many weak acids in presence of oxygen. It is easy to understand how oxygen acts in such cases, but the facts show that the effect produced by "nitric acid" is not so readily interpreted, and their consideration raises important questions of general application.

Russell and Lapraik have shown that when "nitric acid" is freed from nitrous compounds it does not dissolve silver, but that action sets in when a trace of nitric oxide is introduced, and continues with increasing rapidity as the quantity of the nitrous compound—a necessary product of the action—increases; Veley's later experiments have shown that the same is true of copper, without, however, affording any further explanation of the phenomena. Although it is not to be expected that such metals would dissolve in nitric acid even when coupled with a relatively electronegative conductor, as they have negative heats of dissolution, yet if the acid also acted as depolariser a cycle might be formed in which sufficient energy would be developed to condition change; it therefore follows that in such cases nitric acid does not act as the depolariser in accordance with the equation:—



and that in point of fact the nitrous compound is the depolariser, although the nitric acid is the actual solvent of the metal, the hydrogen of the acid being virtually directly displaced by the metal with the assistance, however, of the current energy derived from its own oxidation by the nitrous compound.

But what interpretation is to be given of the behaviour of more active metals, such as zinc, magnesium, &c., which have positive heats of dissolution, and, therefore, are capable of dissolving in the pure dilute acid if coupled with a relatively negative conductor; does nitric acid in their case directly act as depolariser? If it be capable of thus acting, such metals even when uncoupled should dissolve in the pure diluted acid. It is noteworthy that when such metals are dissolved in nitric acid hydrogen is sometimes evolved. It has been suggested that this hydrogen is derived from the interaction of the metal and water, but I cannot now regard this as a probable explanation; its production serves rather to suggest a deficiency of the depolarising agent, which cannot well occur if nitric acid be the depolariser. Indeed, if nitric acid be regarded as directly active, it is remarkable that in presence of the large excess of the acid which is always present any hydrogen should escape; and also that the reduction should extend so far as it often does, and not extend merely to the formation of nitrous acid. If, however, the acid be incapable of directly acting as depolariser, and a nitrous compound be the initially active depolarising agent, it is no longer surprising that

owing to the nitrous compound suffering further reduction it should be deficient in parts of the circuit, and that consequently hydrogen should escape. Why the reduction should extend so much further when metals having positive heats of dissolution are used, however, still requires elucidation.

In the case of sulphuric acid, whatever metals be dissolved in the *diluted* acid, no reduction takes place; and it is only when the concentrated and more or less heated acid is used that sulphurous oxide and other reduction products are obtained. It appears not improbable that reduction only takes place under conditions under which the presence of sulphuric *oxide* is possible, *i.e.*, that depolarisation is effected by sulphuric *oxide* and never by sulphuric *acid*, although this latter may be regarded as the actual solvent of the metal. There is at present no evidence forthcoming to show that nitric acid can dissociate into the anhydride and water, and even if such a change took place in concentrated solutions, there is no reason to assume that it can also take place in dilute solutions, and that this is the explanation of the difference between nitric and sulphuric acids. It is well known, however, that nitric acid is resolved with extreme facility into nitrogen dioxide, water, and oxygen, and that it is excessively sensitive to the action of nitric oxide—a trace of nitric acid would therefore exercise a fermentative action and condition, the formation, it may be, of nitrous acid, or—as there is no evidence compelling us to suppose that the compound represented by the formula HNO_2 exists—it may be of nitrogen dioxide. In this latter case solutions of nitric acid would resemble concentrated sulphuric acid in containing a reducible oxide, and it may be that their depolarising action is initially exerted through such an oxide alone.

To arrive at a clear conception of the function of acids in dissolving metals, and of the nature of depolarising agents, it would, therefore, appear to be necessary to take into account many circumstances to which hitherto but little attention has been paid.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 21, May 23, 1893.

The Chemistry of the Middle Ages.—M. Berthelot.—The author has presented to the Academy a new work which he has just completed. The first volume is a study of the Latin alchemy as far as the 14th century. The Syrian alchemy, forming a connecting link between the Greek and the Arabic authors, is considered in the second volume. This volume includes a translation of the great work of Zosimus, the original of which has been lost and which is now known only from a Syrian version. The third volume is devoted to the Arabic authors, especially Djaber (commonly called Geber). The authentic Arabic writings contain little beyond facts already put on record by the Greeks.

Certain Rare or Novel Natural Phosphates: Brushite, Minervite.—Armand Gautier.—Brushite is a native crystalline calcium biphosphate, which, as obtained from the Minerva caverns, contains neither chlorine nor fluorine. The minerals in which phosphoric acid is united to aluminium, with or without an excess of base, are variscite, callinite, gibbsite, wavellite, Fischerite, peganite, Evansite, and turquoise. Bauxite often contains an appreciable quantity of aluminium phosphate. Gibbsite may even be confounded with hydrargyllite, which contains no phosphoric acid or a mere trace.

Determination of Water in Soils Bearing Different Crops After Prolonged Drought.—M. Reiset.—Wheat may vegetate well and reach perfect maturity in a soil containing only 1.22 grms. water in 100 parts of earth. Grass turf is burnt dead in soils containing 6.8 and 7.84 grms. water per cent.

Election of a Correspondent for the Section of Physics.—Herr G. Widemann (Wiedemann?) was elected *vice* the late Dr. Weber by a large majority. Professor Thalén received only 1 vote!

On Iron Chloroborate and on a Method of Preparing Chloroborates Isomorphous with Boracite.—G. Rousseau and H. Allaire.—The method followed by the authors consists in causing the vapour of a metallic chloride to react at a red heat upon natural calcium borate or preferably upon boro-sodio calcite. Iron chloroborate crystallises in transparent cubes of a greyish colour, and which act upon polarised light.

Heat Liberated in the Combination of Bromine with Certain Non-saturated Substances of the Fatty Series.—W. Louguinine and I. Kablukow.—The authors conclude that the heat liberated in the combination of bromine with the hydrocarbons examined increases as we ascend in the series of the homologues. The presence of an atom of Br replacing H in the non-saturated hydrocarbons retards considerably the speed of the reaction of the addition of bromine. In presence of the group OH the reaction of addition ceases to be definite and is accompanied with a reaction of substitution.

The Licarhodol Derived from Licareol.—Ch. Barbier.—The composition of licarhodol is $\text{C}_{10}\text{H}_{18}\text{O}$. It is a colourless, oily liquid, soluble in water, and giving off a strong odour of roses. Under a pressure of 19 m.m. it boils at 122° ; its specific gravity at 0° is 0.8952, and in a stratum of 0.20 metre and at a temperature of 20.4° it gives a deflection of $-0^\circ 14'$. On oxidation it yields an aldehyd, $\text{C}_{10}\text{H}_{16}\text{O}_2$.

Action of Sodium Sulphite on the Salts of the Amidophenols. New Method of Obtaining Amidophenols from the Salts.—Aug. Lumière and A. Seyewetz.—The authors have succeeded in isolating several amidophenols in a pure state by utilising for the decomposition of their salts a substance with a weak alkaline reaction, the neutral sodium sulphite, which in consequence of its reducing properties prevents the oxidation of the base formed.

Ptomaine Extracted from the Urine of Patients Suffering from Eczema.—Dr. A. B. Griffiths.—This base, the extraction of which was described in the *Comptes Rendus*, cxiii., p. 656, is white, crystalline, soluble in water, and of a faintly alkaline reaction. It forms a hydrochlorate, a chloroplatinate, and a chloraurate, all crystalline; it gives a brown precipitate with phosphotungstic acid, yellowish with phosphomolybdic acid, yellow with picric acid, and yellowish with silver nitrate. With mercuric chloride it gives a greenish precipitate. It is also thrown down by Nessler's reagent. The composition of the base is $\text{C}_7\text{H}_{15}\text{NO}$. It is poisonous. A solution of this ptomaine (in sterilised water), if injected under the skin of a rabbit, produces a catarrhal inflammation at the point of injection, a strong fever, and finally death. This ptomaine, which the author names eczemine, is not found in normal urine.

On δ -Achroglobine: a Respiratory Globuline contained in the Blood of some Mollusca.—Dr. A. B. Griffiths.—The author has formerly described three colourless globulines which possess the attributes of oxygenation and dis-oxygenation. They are:— α -achroglobine in the blood of Patella, β -achroglobine in the blood of the Chitons, and γ -achroglobine in the blood of the Tunicata. He has obtained a fourth similar compound from the blood of some species of Doris, and has named it δ -achroglobine. Its analysis leads to the formula $\text{C}_{659}\text{H}_{792}\text{N}_{165}\text{SO}_{153}$. It exists in two states, oxidised and

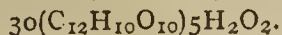
reduced. 100 grms. of this respiratory globuline absorb 125 c.c. of oxygen at 0° and under a pressure of 760 m.m. If dissolved in a dilute solution of magnesium sulphate, its specific rotatory power for the ray D is $[\alpha]_D = -54^\circ$. With CH_4 it forms a yellowish compound, with C_2H_2 a greenish compound, with C_2H_4 a brownish compound. These compounds are dissociable in a vacuum.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. ix. and x., No. 9.

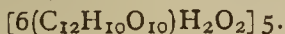
Synthesis of Erythrite.—M. Griner.—This paper is the subject matter of a "pli cacheté" deposited with the Society on March 24, and opened on April 14. On saponifying at 100°, by means of baryta water the triacetate obtained from dibromdiacetate, the author has produced a compound which melts at 118° and which presents all the characters of natural erythrite.

On Certain Substituted Carbides of Benzene.—P. Genviess.—In this research the author has determined the combustion and formation heats of propylbenzene, isopropylbenzene, normal propyltoluene, and isopropyltoluene. He has established the constitutional formulæ of di-isopropylbenzene, normal propyltoluene, and isopropyltoluene. He has prepared two propylbenzenes monochlorised in the lateral chain, and determined their constitutional formulæ. He has obtained an isopropylbenzene, monochlorised in the nucleus, and seen the position of the chlorine. He has lastly shown that by the action of chlorine in heat it is possible to obtain a propyltoluene chlorised in the lateral chain, and has determined its constitution.

On Inuline.—C. Tanret.—The substance hitherto known as inuline is a mixture of two or three substances, the proportions of which differ according to the method of preparation. Its composition approaches—



When air-dried it may be represented as—



Over sulphuric acid it loses its water very slowly. Inuline is deposited from its solutions in water in irregular granules of from 0.0005 to 0.002 m.m. in diameter, and from its alcoholic solutions in nearly globular granules, the larger the greater the quantity of alcohol used. With one volume of alcohol they may reach 0.008 m.m., and which have no appreciable action on polarised light. Inuline does not swell up in water. It is very sparingly soluble in cold water (not in 10,000 parts of water at 15° after agitation for several days). It is very soluble in boiling water. In cold dilute alcohol it is insoluble, but dissolves freely with the aid of heat. At 178° it melts, becoming yellow, slightly acid, and very soluble in cold water. At a slightly higher temperature it becomes strongly acid, and is converted into pyroinuline. The specific gravity of inuline dried at 130° is, according to the author, = 1.539, and that of the hydrated compound = 1.478. The rotatory power for inuline dried at 130° is $\alpha_D = -39.5^\circ$. This rotatory power is influenced neither by temperature nor by the concentration of its solutions. Inuline heated with dilute acids does not yield simply levulose, but a mixture of about 12 parts of levulose to 1 part of glucose. Cold baryta water dissolves inuline at first, but a further addition gives a precipitate. Iodine does not colour inuline at all. It does not reduce Fehling's liquid, and has no reaction upon beer-yeast or diastase.

On Dipropylamidoacetic (Dipropylaminoethanoic) Acid.—F. Chancel.—The author has prepared this acid, to which he ascribes the composition $\text{C}_8\text{H}_{17}\text{NO}_2$. He has also obtained its compounds with hydrochloric acid, its chloroplatinate, chloraurate, and its copper salt. To the last-mentioned substance he assigns the composition $(\text{C}_8\text{H}_{16}\text{NO}_2)\text{Cu} + \text{H}_2\text{O}$.

On Acetic Tripropylbetaine (Ethanoyltripropyl-taine).—F. Chancel.—This body is obtained by the action of ethyl monochloracetate upon dry tripropylamine. The author has examined this substance, its hydrochlorate, chloroplatinate, chloraurate, and picrate, as also ethyl-tripropylaminoethanoate, chloroplatinate, and chloraurate.

On Dipropylcyanamide and Dipropylcarbodiimide.—F. Chancel.—The former of these compounds, $\text{C}_7\text{H}_{14}\text{N}_2$, is a mobile liquid of the specific gravity 0.88 at 0°, of a burning taste, and an aromatic odour. It boils at 107° under a pressure of 21 m.m., at 220° under 770 m.m. It is insoluble in water, soluble in alcohol and ether, and does not solidify at -50° . Dipropylcarbodiimide is a mobile liquid of the composition $\text{C}_7\text{H}_{14}\text{N}_2$. It boils at 80° under a pressure of 28 m.m., and at 171° under 765 m.m. It does not solidify at -50° . It is insoluble in water, but soluble in alcohol and ether.

MISCELLANEOUS.

The Royal Society and Trade Certificates.—The subjoined expression of opinion was adopted by the President and Council of the Royal Society at their meeting on May 18, and was ordered to be communicated to all the Fellows of the Royal Society:—

"The attention of the President and Council of the Royal Society has been called to certain advertisements appearing from time to time in the public newspapers and in various trade journals and circulars, containing certificates and statements signed by Fellows of the Society. These certificates and statements are not in all cases confined to mere analyses or simple matters of fact, but occasionally include expressions of opinion as to the subject matter of the advertisements, and laudatory passages which assume much of the character of an advertiser's encomium. The President and Council fully recognise the liberty of the Fellows to give, when consulted, authoritative statements on chemical analysis or any other scientific facts on which they are called upon to advise. They feel, nevertheless, that in some of the trade certificates already mentioned, due regard has hardly been paid to the status and dignity of the Royal Society, and they are of opinion that the issue of such certificates tends to act injuriously upon the reputation of the Society. They are, however, confident that when attention is called to the subject, all the Fellows will endeavour to express any statements relating to matters of trade or manufacture in such terms that no suspicion of mercenary motives or commercial partisanship can possibly attach to them."

Photographic Competition.—We beg to call attention to the advertisement of Messrs. Perken, Son, and Rayment, who are offering prizes for the best sets of photographs taken with their "Optimus" lens.

Instruction in Dyeing at Aix-la-Chapelle.—With the commencement of the winter term a new special school for dyeing will be opened in connection with the local polytechnicum. All the appliances will be adapted to the most recent advances in the tinctorial art.—*Chemiker Zeitung*.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Grinding and Polishing Quartz.—(Reply to "Amateur.")—Formerly quartz was cut on a lead wheel with emery and water, and polished on a zinc wheel with putty of tin and water. This process may perhaps suit your correspondent.—WM. BROWN, 14, Dale Street, Liverpool.

MEETINGS FOR THE WEEK.

WEDNESDAY, 21st.—Geological, 8.

Meteorological, 7.

Microscopical, 8.

THURSDAY, 22nd.—Royal Society Club, 6.30. (Anniversary).

FRIDAY, 23rd.—Physical, 6. Exhibition of a Form of Carey-Foster Bridge, by Mr. Nalder. An Influence Machine, by Mr. Pidgeon. An Influence Machine, by Mr. Wimshurst. A New Volumenometer, by Mr. Myers.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1752.

ON THE METALLURGY OF LEAD.*

By J. B. HANNAY, F.R.S.E., F.I.C.

IN this paper the author details the results of seven years' researches on the metallurgy of lead.

It was found that all the information given in the chemical authorities was erroneous, and every point had to be made the subject of a special study.

The subject is divided into the following sections:—

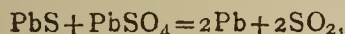
1. The relations of lead and sulphur.
2. Specific gravity of sulphide of lead.
3. Methods of analysis.
4. Furnace reactions of lead compounds.
5. Lead smelting.
6. New metallurgy of lead.

It is shown that all mixtures of lead and its sulphide, or what may be called subsulphurised lead, can be fractionated into the two extreme terms, metallic lead and its monosulphide, by simply melting and crystallising out the higher sulphurised portion, as the sulphur tends to form monosulphide, which crystallises out and leaves a lead poorer in sulphur as the "mother liquor." This process may be carried on till pure metallic lead is left.

It is then shown that the accepted specific gravity of sulphide of lead is too low, as it oxidises when pulverised and boiled with water, and instead of being 7.585, it is 7.766, and a curve is constructed of the specific gravities of all sulphurised compounds of lead from PbS to Pb.

The methods of analysis are examined, and shown to be fallacious, and a more reliable method devised.

The formula given for the reaction going on in the reverberatory furnace when lead is smelted, viz. :—



is shown to have no existence in fact, as when sulphide and sulphate of lead act upon each other a volatile compound PbS_2O_2 is formed, which introduces complications, and the reaction takes a different direction. The discovery of this compound supplies the explanation of the question, "Why does galena form a fume in the air when it is absolutely fixed in nitrogen and hydrogen?"

A series of volatile compounds of one molecule of PbS with a molecule of CO_2 , H_2O , SO_2 , and CO , is shown to exist.

These compounds are unique amongst combinations between solids and gases, as they are only stable at a red heat and dissociate on cooling, which is the reverse of the behaviour common to such compounds.

All the reactions involved in furnace reactions of lead, its oxide, sulphate, and sulphide, are then traced from their beginning to the final products, as well as the reaction of sulphate and silicate with carbon, and the decomposition of sulphite of lead by heat. The knowledge so gained is applied to lead smelting, and this is shown to be really a fractionation of a low sulphide into lead and its sulphide accompanied by rapid oxidation with the formation of an oxysulphide PbS.PbO , which is the basis of black and grey slags. The operations involved in smelting are shown to be explainable by the new reactions discovered, and Percy's remark that the chemistry of lead smelting was still unexplained is shown to be no longer applicable.

It is pointed out that the new knowledge enables us to map out a new metallurgy of lead, by which we are enabled to avoid the formation of the oxysulphide which

forms slag, and to turn the troublesome volatile oxysulphide, which forms fume, to useful account. The silver can be eliminated, and any proportion of lead, its sulphate, or oxide, formed direct from galena.

Some of the curious crystalline forms of lead sulphide which have been observed during these researches are shown, one of which illustrates very clearly the fractionation of a low sulphide into lead and the monosulphide.

BLACK VARIETY OF ANTIMONY TRISULPHIDE.

By C. A. MITCHELL, B.A. (Oxon).

THE following quick method of preparing the black variety of Sb_2S_3 may be found useful as a lecture experiment:—

About 5 grms. of Sb_2O_3 are dissolved in about 30 c.c. of HCl (two parts of acid to one of H_2O), and H_2S passed in to saturation. The liquid with the orange sulphide in suspension is then kept boiling over a Bunsen, while a current of CO_2 is passed through. In the course of a few minutes a good deal of the orange precipitate dissolves, while some falls down as the black sulphide. By again passing H_2S through the liquid and repeating the above process, more may be converted into the black variety, and by continued repetition the whole may be thus transformed in a short time.

Analysis of this black sulphide shows a percentage of antimony corresponding to that required by the formula Sb_2S_3 .

King's College Laboratory.

THE FLASH-POINT AND POINT OF DANGER IN MINERAL OILS.

By D. R. STEUART, F.I.C., F.C.S.

THE danger of fire or explosion from a mineral oil is tested by taking its flash-point. The Government test of Professor Abel is a 2-inch cup covered on the top. The filling, heating, light applied, &c., are all defined. Holes are opened in the lid for a moment to apply the light at specified intervals, and the point got is very definite. The question is: What relation has the point so got to the point of danger? Is the Abel flash-point itself the point of danger, or is danger to be feared only at a much higher temperature?

Before a Parliamentary Committee some years ago, a witness said there was no danger at all until the temperature of the American fire test. The flash-point is the lowest temperature at which the vapours and air give a little explosion when the light is applied, going instantly out. The fire-point is the lowest temperature at which the vapours burn continuously.

A particular sample of oil I tested flashed in Abel test at 78° F., in the old Government open test at 105°, and fired in the old Government open test apparatus at 122°. This last is something like the American fire test. Is there, with this oil, no danger of fire in a store or explosion in a lamp until about 120° F. is reached?

A moment's thought will satisfy us that although a little cup of oil cannot supply sufficient vapour to keep up a constant flame until 122° F. is reached, a larger surface will supply vapour, and, when ignited, heat, enough to produce a constant flame at a much lower temperature. I tried the oil mentioned above in an apparatus like the old Government open test, with screen around and partly also on the top, but 9 inches in diameter. Applying a small flame every two degrees at a half-inch above the surface, the oil ignited explosively at 88° and continued

* Abstract of a Paper read before the Royal Society.

to burn furiously. Repeating the experiment, and applying the flame at every degree, it ignited and burned continuously at 87° , and the flame rapidly increased in vigour. Making the same apparatus a close test like Abel's, the oil ignited and fired (burned continuously) at 76° F.; that is with a 9 inch wide closed test, instead of the 2 inch prescribed by act of Parliament, the oil not only flashed but fired two degrees below the flash point Abel test, and when open it fired only nine degrees above the Abel test. With a wider surface of oil, the flashing and firing would no doubt take place at even a lower temperature. These experiments prove, if they require proving at this time of day, that the old Government open test and the American fire test are altogether deceptive, and that in store, barrel, or tin can, the flash-point Abel test is a point of real danger, and that for oil in large masses the danger begins even below the flash point (Abel). The experiments also prove that, except for very small surfaces of oil, the flash-point and the fire-point are the same.

The following happened in my experience :—

A large tank of very high flashing oil was being pumped into, and the oil therefore in considerable commotion. The temperature was far below the flash-point in Abel cup; nevertheless, vapours were evolved and filled the top of the tank, and, expelled by the rising oil, overflowed out at a manhole door on the top which was not quite close, and ignited at a lamp some distance below. The fire ran up the stream of vapour; there was an explosion, blowing off the top of the tank, and the oil caught fire and burned uncontrollably until it was practically all consumed. For danger in oil works, even the Abel flash-point is deceptively high. Is it because this has not been realised that fires in oil works have been so frequent?

In regard to danger in a lamp, in 1872 before a Select Parliamentary Committee, a chemical expert said:—"We have made a great number of experiments to ascertain whether oils which flash at 100° (equivalent to 73° Abel test) or even a little below 100° , can by any contrivance be exploded in a lamp, and we cannot do it; whether by electric spark or by flame of any kind, but we cannot fire it; that we have ascertained to be a fact." Now the real fact is that a lamp filled with oil of 100° old open test, if shaken up—as by carrying the lamp—can be exploded with electric spark quite easily, even at 73° . The explosion is not violent; but at 5° above the flash-point (Abel) the explosion may be very violent. Such an oil can explode violently at any temperature between 78° and 120° ; that is, at all temperatures lamps are generally exposed to. For lamps burning heat up the oil, more with large lamps than with small, more with metal lamps than with porcelain, more if with metal safety tubes than without, and more with flat burners than with central draught. As all ordinary lamps are more than two inches wide, the flash-point in them will be the Abel flash-point or a little lower. There is a little danger even at the Abel flash-point, for although the explosion at that temperature is a mere puff, yet if it happened while the lamp was being carried it might cause it to be thrown down on combustible material. At any rate, at five degrees above the Abel flash-point the danger is very great.

I have tried many experiments upsetting cheap glass lamps when burning so as to break them. I had the lamp half filled with oil and heated to certain definite temperatures. At 5° above the flash-point (Abel) all in general went out. At 10° above flash-point with some low flashing (73° to 78°), petroleum ignited and burned vigorously, and some merely flashed and went out. High flashing oils (100° to 110° Abel), 10° above flash point invariably went out or merely flashed; they never permanently ignited. At 15° above the flash-point the high flashing oils inflamed, but burned quietly, and the fire could easily have been commanded. So low flashing oils may be a great danger if overset at 10° above flash-point; but high flashing oils are not in great danger until 15° over flash-point or more; that is, if overset on an ordinary floor. If overset on easily combustible materials, there is great danger, even

at the flash-point, and as the absence of combustible materials cannot be depended on, even for this kind of accident, the flash-point (Abel) becomes the point of danger. If an open cup of oil heated to the flash-point (Abel) has a large lighted candle plunged into it, the candle is extinguished just as by water. These experiments show the freedom from danger in lamp, or in any small quantities, and particularly of high flashing oil, if kept several degrees under the Abel flash-point.

High flashing oils burn practically as coolly as low flashing oils, and if we seek safety by using a high flashing oil we are not running into any other danger.

Coroner's inquests are very frequent on lamp accidents. It has become the custom for the inspectors to state that no dangerous oil is now imported into England, and inspector and coroner put the whole blame on the lamp. But surely no scientific man is free to state that 73° flashing oil is safe in our climate. It is often 80° or over it in houses, and all the year round the temperature in ordinary lamps is 80° to 90° . The danger is not a mere matter of opinion, but an easily ascertainable scientific fact; and when a scientific man makes such a statement regarding a matter involving hundreds of deaths in England every year, I think he should somehow be amenable to the ban of the profession, if to nothing else. It is absurd to condemn the poor for not having safety lamps; besides, even if they had them, they are only an extra source of danger unless in proper order, and with cheap lamps and ignorant people that could not be depended on.

It is obvious to common sense that the poor should be supplied with oil, such as the rich supply themselves with, safe to work with at ordinary temperatures, and perfectly safe from danger of explosion in ordinary lamps properly attended to. With ordinary petroleum there are many real lamp explosions, in spite of all that is said to the contrary. Carry the lamp about, attempt to blow it out, or turn down the wick too far, and the lamp explodes. These could never happen with an oil whose flash is a few degrees above the temperature of the oil in the lamp. Lamp fatalities are so dreadful that one would think that a few would waken up the people so as to get the matter put right; but the deadly tale goes on day by day, but it is among the very poor, and nobody seems to care. The Government, contrary to the example of all other civilised countries, has given what is practically a certificate of safety for oils flashing above 73° , and, instead of protecting us, has, by legislation, shut itself out from the power of interfering. So these dangerous oils can be stored in any quantity anywhere. Store proprietors and railway companies exercise great care; nevertheless, our lives are at the mercy of the idiosyncrasy of individuals, and we may expect a catastrophe on the grand scale some day.

In the past, nobody took any interest in the petroleum laws except the representatives of the oil trade. It is time scientific men, for the sake of the voiceless poor, should pay some attention to the matter. The science put before the Parliamentary Committee was sometimes of a strange kind, and matters of fact were treated as matters of opinion instead of being settled by experiment. It is evident the Government does not know that the flash-point (Abel) is in all cases a point of real danger, and in stores and tanks of great danger. They evidently think there is no danger until the temperature of the old open test. They would never have lowered the safety-point from 100° to 73° if they had known that the old test was deceptive by that interval—and they ought to have known.

Oil vapours when hot, as in the old open test, diffuse away pretty rapidly, but when cold, as in a store, they are very heavy, roll along to the lowest point, and if there are no air currents diffuse away very slowly. They can be decanted from vessel to vessel like carbonic acid gas; but this the Government officials are ignorant of, and think that oil vapours diffuse rapidly into the atmosphere like coal gas.

A little attention by scientific men to our petroleum laws would even cause them to be altered so as to do away with our present horrors and terrors. The development of this great trade on safe lines, in conformity with physical and moral law, would bring a great and immediate blessing to the people, and very soon a great advantage to manufacturers and the trade.

THE EXAMINATION OF PAPER FOR METALLIC PARTICLES.

By CLAYTON BEADLE.

PAPER frequently contains particles of impurities that are difficult to identify even under the microscope. They are frequently metallic iron derived from the iron tanks, beaters, &c., in which the pulp has been treated, and brass derived from the wearing down of the beater bars, and, in the case of rag-papers, from the buttons.

The presence of these metallic particles is often the means of spoiling large quantities of paper, and a ready means of their detection is to be welcomed by paper-makers. The following I have found of great service:—

Strips of the suspected paper are floated in a 1 per cent solution of potassium ferrocyanide acidified with a few drops of nitric acid. After three hours' treatment, particles of iron will be rendered evident by the production of deep blue spots, and brass by chocolate-coloured spots. The former are very satisfactory, but the latter may easily be mistaken for other foreign matter contained in the paper.

To confirm the presence of brass particles I place a bead of silver nitrate solution on the suspected spots, and examine them under the microscope by reflected light. If any brass is present clusters of crystals of metallic silver will soon be seen forming themselves on the surface of the paper. After the solution has nearly dried into the paper, a drop of potassium ferrocyanide solution is placed close to the margin. On diffusion it produces a chocolate colouration about the margin. Other metallic particles are seldom met with.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1893.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, June 7th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to

oxidise the organic matter in all the samples submitted to analysis.

The character of the water supply to the metropolis during the month of May continued to be in all respects entirely satisfactory. The proportion of organic matter present, as indicated by the estimations of organic carbon, of oxygen required for oxidation, and of the colour tint of the water, was exceedingly minute, the mean results of these estimations, in the case for example of the Thames-derived samples, being identical with those afforded by the previous month's supply already commented on for their exceptional lowness, as shown in the following Table:—

1893.	Ratio of brown to blue tint.	Oxygen required for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Means.	Maxima.
April	11'9 : 20	0'28	0'088	0'125
May	11'3 : 20	0'29	0'089	0'124

No appreciable difference was noticeable in respect to the proportion of common salt, about one and a half grain per gallon, present in the water in flood time and during the present dry period; but, as shown in the following Table of Thames water results, the proportions of oxidised nitrogen and the degree of hardness underwent during the later months, probably from the increasing activity of fluvial vegetation, a steady and appreciable decrease.

1893.	Common salt per 100,000.	Nitric acid per 100,000.	Degrees of hardness per gallon.
February	2'242	0'952	17'56
March	2'167	0'931	16'80
April	2'181	0'888	15'11
May	2'196	0'611	14'66

All of the 182 samples examined during the month were found to be clear, bright, and efficiently filtered.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

FIRST PAPER: THE ANALYSIS OF BARIC BROMIDE.

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 284).

Data and Results.

THE first column of the final Table of Data gives the number of the experiment. The second column contains the weight of the crystallised baric bromide, while the third contains the observed weight of the ignited baric bromide. After this is recorded the number of c.c. of standard hydrobromic acid (of which one litre corresponded to a grm. of silver) required to restore the small amount of bromine lost during ignition. This quantity is divided into two parts, the upper one corresponding to baric hydroxide, and the lower to baric carbonate. Multiplying the upper figure in this column by $\frac{108}{100}$ m.grm., and the lower figure by $\frac{50}{100}$ m.grm., and adding the two products to the weight given in column III., we obtain the corrected weight of the baric bromide, which is recorded in the fifth column. The sixth column gives the total weight of silver taken; the seventh, the number of c.c. of the same hydrobromic acid necessary to titrate back to the mean end point; and the eighth, the weight

* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

TABLE OF DATA.—(All weights are corrected to the Vacuum Standard).

I. No. of Analysis.	II. Weight of Crystallised Baric Bromide. Grms.	III. Observed Wt. of Anhydrous Baric Bromide. Grms.	IV. HBr solution to Neutral Alkali. C.m. ³	V. Corrected Wt. of Anhydrous Baric Bromide. Grms.	VI. Total Weight of Silver. Grms.	VII. HBr solution to titrate back. C.m. ³	VIII. Weight of Silver corresponding to BaBr ₂ . Grms.	IX. Total Weight of Argentio Bromide. Grms.	X. Argentio Bromide corres- ponding to BaBr ₂ . Grms.	XI. Sample of Baric Bromide used.
1	2.56714	2.28760	—	—	1.66314	2.40	1.66074	2.89444	2.89026	I.a
2	3.89534	Not ignited.	0	3.4712	2.52554	5.35	2.52019	4.39566	4.38635	I.a
3	—	3.80860*	{ 1.90 2.50	3.81086	—	0.30	—	4.81740	4.81688	I.b
4	—	2.19830*	{ 1.65 0.25	2.1994	1.59832	1.45	1.59687	—	—	I.b
5	—	2.35954	{ 0.12 0.22	2.35971	1.71613	2.90	1.71323	2.98735	2.98230	I.c
6	3.30433	2.94178	{ 0.32 0.22	2.94207	2.13889	3.05	2.13584	3.72340	3.71809	II.a
7	1.80930	1.61177	{ 0.16 0.11	1.61191	1.17100	0.80	1.17020	—	—	II.b
8	2.36427	Not ignited	0.00	2.10633	1.53056	1.35	1.52921	2.66426	2.66191	II.b
9	—	2.91650	{ 0.32 0.26	2.91682	2.11840	1.00	2.11740	3.68789	3.68615	II.c
10	2.66363	2.37226	{ 0.38 0.90	2.37290	1.72298	0.22	1.72276	2.99906	2.96868	III.
11	2.07483	1.84804	{ 0.14 0.00	1.84822†	1.34328	1.65†	1.34175†	2.33797	2.33530†	III.
12	—	1.9038	{ 1.40 0.00	1.9046	—	0.37	—	2.40798	2.40733	IV.b
13	2.75591	2.45417	{ 3.06 0.30	2.45611	—	—	—	—	—	IV.a
14	6.35791	Not ignited	0.00	5.66647	4.12090	7.30	4.11360	7.1739	7.1612	IV.a
15	3.95705*	3.52610*	{ 0.35 0.85	3.5267	2.56100	0.90	2.56010	4.4583	4.4567	IV.a
16	4.8442*	4.3161*	{ 0.00 1.75	4.3169	3.13550	1.20	3.13430	—	—	V.
17	3.78040*	3.36557*	{ 0.15 1.50	3.36635	2.44567	1.82	2.44385	—	—	VI.b
18	3.22971	Not ignited	0.00	2.87743	—	0.54	—	3.63738	3.63644	VI.a
19	3.88750	3.46330	{ 0.03 0.32	3.46347	2.51529	1.14	2.51415	4.37867	4.37669	VI.a

* Corrected for small amount of baric sulphate (or silica) found on solution.

† See ante, p. 284.

N.B.—Two weights (the argentic bromide of Analysis 4 and the silver of Analysis 18) are omitted from this Table, as they were known to be in error. It might have been well to omit the whole of the twelfth experiment for the same reason. The other blanks were never filled.

of the silver corrected by subtracting from the weight given in column VI. the amount of silver corresponding to the quantity of acid given in column VII. In the same way, the ninth and tenth columns contain respectively the total and the corrected weight of argentic bromide. Hence the weights actually used in the calculation of the results are those recorded in columns V., VIII., and X.

The discussion of the results is simplified by reducing all the amounts of baric bromide to the basis of 100.000 parts of silver, and the corresponding quantity, 174.080 parts, of argentic bromide. The water of crystallisation is included in the following Table only because the calculation of Analyses 2, 8, 14, and 18 depends upon the knowledge of its amount. The great variations noticeable in the results for the water of crystallisation are due to the varying circumstances attendant upon the crystallisation, to the fineness of the powder, and to the hygroscopic condition of the air at the time of weighing the crystals. Hence for the present purpose it was possible to compare only like samples which had been weighed out under like conditions. Analyses 13 and 15 show that in this way perfect constancy can be reached. This

part of the work has of course no other bearing upon the atomic weight of barium.

The first two experiments were merely preliminary, and are not included in the final average. Most of the variations evident in the earlier experiments were undoubtedly due to unfavourable conditions existing in the laboratory during the year 1891–92. In the autumn of the latter year the laboratory was completely and most admirably remodelled, through the kindness of the Corporation of the University, and the last seven experiments were performed under conditions as favourable as could be desired.

The presence of any of the most likely metallic impurities—strontium, calcium, potassium, or sodium—would tend to lower the observed values recorded in the third and fourth columns of the Table of Results, and hence the atomic weight of barium. Chlorine would lower and iodine would raise the values given in the third column, but neither would have much effect on those given in the fourth column. The best possible proof of the freedom of the preparations from these two impurities, as well as of the purity of the silver, is to be found in the

TABLE OF RESULTS.

No. of Anal.	Salt employed.	Parts of Baric Bromide corresponding to 100,000 parts Silver.	Parts of Baric Bromide corresponding to 174,083 parts Argentic Bromide.	P.c. of Silver in AgBr.	Water of cryst. in Baric Bromide.
1	I.a	137.746	137.783	57.460	10.889
2	I.a	137.736	137.760	57.455	
3	I.b		137.723		
4	I.b	137.732			
5	I.c	137.735	137.739	57.447	
6	II.a	137.748	137.748	57.445	10.964
7	II.b	137.747			10.910
8	II.b	137.740	137.747	57.448	
9	II.c	137.755	137.748	57.442	
10	III.	137.738	137.752	57.451	10.915
11	III.	137.747	137.772	57.455	10.922
12	IV.b		137.726		
13	IV.a				10.878
14	IV.a	137.750	137.745	57.443	
15	IV.a	137.756	137.754	57.445	10.875
16	V.	137.731			10.885
17	VI.b	137.748			10.953
18	VI.a		137.745		
19	VI.a	137.759	137.758	57.445	
Aver., omitting Expts. 1 and 2 ..		137.745	137.747	57.448	
Average of last seven Expts. ..		137.749	137.751	57.444	
Stas found				57.445	

series of results giving the per cent of silver in silver bromide, tabulated in the fifth column of the Table of Results (*Proc. Amer. Acad. Arts and Sciences*, xxv., 212). The presence of water in the ignited baric bromide would naturally tend to raise the figures given in both the third and fourth columns; the arguments indicating the absence of this insidious impurity were discussed at length in the first part of the paper (see *ante*).

The agreement between the individual results is as close as could reasonably be expected, when one considers the small amounts of material used in some cases. It may be concluded, then, that a hundred parts of silver correspond to about 137.747 parts of anhydrous baric bromide, no matter what may be the method used for its preparation. If the salt contains an impurity, it is strangely constant in amount.

The Atomic Weight of Barium.

From the results which have just been given, the atomic weight of barium is very readily computed. In the following Table are given the values corresponding to the three standards at present in use.

From the Ratio of Silver to Baric Bromide.

If silver=107.93, and bromine=79.955, barium=137.426
If silver=107.66, and bromine=79.755, barium=137.083
If silver=107.12, (oxygen=15.88), barium=136.396

Greatest variations from the mean, $\begin{cases} +0.030. \\ -0.040. \end{cases}$

From the Ratio of Argentic Bromide to Baric Bromide.

If argentic bromide=187.885, barium=137.431
If argentic bromide=187.415, barium=137.089
If argentic bromide=186.476, barium=136.401
Greatest variation from the mean, ± 0.054 .

It is not very difficult to explain the reason for the difference between this new value, 137.43, and the old one, 137.10. The incomplete knowledge regarding the end point of chlorine reaction in 1858 is probably responsible for a part of the difference, and a portion more may possibly be explained by the impurities which were assumed to be inessential. But it has already been said that a discussion of the results of thirty-five years ago can be of little value. The only true solution of the question is the experimental one. In the near future I hope to continue the investigation which is herewith commenced, as well as to begin a similar research upon strontium and calcium.

THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.
(Continued from p. 261).

Manganese.

Two grms. of the sample, contained in a beaker, are treated with 50 c.c. of nitro-hydrochloric acid, and gently heated until the iron has dissolved. The solution thus obtained is transferred without loss to a flask of 2½ litres capacity, diluted with water until the volume occupied measures 1½ litres, and heated to nearly a boiling temperature. The next step is to precipitate the iron existing in the solution as ferric chloride, which is accomplished by cautiously adding ammonia (sp. gr. 0.88) until it remains slightly turbid, after well agitating the containing vessel. Instead of employing ammonia throughout, it is advisable, as the solution approaches neutrality, to substitute for it a dilute solution, about 1 part in 20 of water. To the slightly turbid liquid add 250 c.c. of hot ammonium acetate, bring it to boiling point, and allow it to stand until the brick-red precipitate of basic acetate of iron has settled. Pass the solution, together with the precipitate, on to a large English filter-paper, and thoroughly wash with hot water containing a little ammonium acetate.† Sometimes, owing to the incomplete precipitation of the iron, a perfectly clear filtrate is not always obtained. This, however, is rather to be desired than otherwise, as the probability of the iron carrying down with it small portions of the manganese is much less than where the precipitation is complete. Should such be the operator's experience, the filtrate is heated to boiling for five minutes, when upon re-filtering it will be found to run through clear.

To facilitate the precipitation of the small quantity of manganese contained in the bulky filtrate, it is concentrated by evaporation until it occupies a volume of 400 c.c. The concentrated solution is now thoroughly cooled, and when this is effected bromine is added until it is of a dark brown colour. This reagent is added in small quantities at a time, and the containing vessel well agitated with each addition. To this brown coloured solution strong ammonia (sp. gr. 0.88) is added until strongly ammoniacal, when it is heated to boiling, and the resulting precipitate of hydrated peroxide of manganese collected on a filter, well washed with water, converted by strong long-continued ignition at a high temperature into tri-manganic tetraoxide, Mn_3O_4 , every

* From *Industries*.

† The details of the method as here given must be strictly adhered to.

hundred parts of which are equivalent to 72.05 per cent manganese, and weighed. The manganese precipitate often contains a small quantity of iron, and as its presence would impair the accuracy of the determination, it becomes necessary to test the Mn_3O_4 , after weighing, for the metal, and if any be found, the amount determined and deducted from the weight of the precipitate. With this object, dissolve the Mn_3O_4 in a small quantity of hydrochloric acid, withdraw a drop of the solution on the end of a glass rod and bring in contact with a drop of sulphocyanide of potash spread on a white porcelain slab. A pink colouration is formed varying in intensity in proportion to the amount of iron, if any, present.

Two methods, either gravimetric or colorimetric, may be employed for the quantitative determination of the iron; of the two, the latter is preferable. In using the gravimetric method, the hydrochloric acid solution of the Mn_3O_4 precipitate is diluted with six times its bulk of water, made neutral with ammonia, and the iron thrown down by the addition of a small quantity of hot ammonium acetate; the solution is boiled, the precipitated basic acetate of iron collected on a filter, washed, converted by ignition into ferric oxide, Fe_2O_3 , and weighed, which weight is deducted from that of the Mn_3O_4 . If Parry's colorimetric method is employed, the manganese precipitate, &c., is dissolved in nitric acid with a few drops of hydrochloric acid. The solution is then transferred to a Nessler's cylinder, four drops of a weak solution of sulphocyanide of potassium added, and cold water is afterwards added until the volume occupied measures 50 c.c., and thoroughly mixed. The colour of this solution is now compared with that produced by taking various quantities of a solution containing a known quantity of iron, adding four drops of sulphocyanide of potassium, and making up with water to a volume occupying 50 c.c., until equality of tints is arrived at. The iron, equal to the number of c.c. of the "standard" solution required, is calculated into ferric oxide, Fe_2O_3 , by multiplying by 1.429 and deducted from the weight of the Mn_3O_4 precipitate. The "standard" solution of iron is prepared of such a strength that a litre contains one gram of the metal. A steel of known composition may be employed; assuming that it contains 99.5 per cent of iron, a solution containing one gram of iron is obtained by dissolving 1.005 grms. in a small quantity of HNO_3 (1.20 sp. gr.) and diluting to a litre. This colour test is also used for the determination of small quantities of iron in blast furnace slags, &c.

Iron is not the only metal which may be contained in the manganese precipitate, as copper or nickel present in the iron or steel would be partly thrown down with it. Its removal may be effected either in the original acid solution of the metal or from the Mn_3O_4 precipitate after weighing. The separation of the copper, &c., in the original solution of the iron or steel will be described under the determination of that metal.

Under certain conditions, potassium chlorate precipitates manganese as black peroxide from a nitric acid solution of the iron and steel. This forms the principle of a method—a combination of the bromine and potassium chlorate method—which furnishes very good results in a much shorter time than the one just described, and allows of a larger quantity of the metal being operated upon. For analysis, 4 grms. of the sample contained in a conical or small flask are digested with 60 c.c. of nitric acid (sp. gr. 1.20) at a gentle heat until the whole is dissolved, when 30 c.c. of nitric acid (1.42 sp. gr.) are added. This solution is heated to boiling, and while at this temperature 6 grms. of potassium chlorate added, a few crystals at a time. After boiling for a period of fifteen minutes, a further addition of the same quantities of acid and potassium chlorate is made, and the solution again brought to, and kept at, boiling temperature for the same period. The solution is now thoroughly cooled, diluted with cold water, and allowed to stand until the precipitated black oxide of manganese, containing also a little iron, has completely settled, when the supernatant liquid

is passed through a Swedish filter without throwing on the precipitate. The small quantity of the manganese oxide which has accidentally passed on to the filter is dissolved in hydrochloric acid, receiving the solution in the vessel containing the bulk of the precipitate, which is also dissolved by the addition of a further quantity of acid and the application of a gentle heat. The resulting solution is now diluted with 200 c.c. of water, the iron carefully precipitated as basic acetate, with ammonia and ammonium acetate, separated by filtration, and the manganese contained in the filtrate precipitated with bromine as previously described. We find this method preferable, for practical work, to that given by M. Troilus, in which the manganese peroxide precipitate is carefully washed until free from iron, and the manganese determined either by direct weighing or a volumetric method.

Spiegel and ferro-manganese may be very well done by the acetate method, or by the volumetric determination of the iron, allowing 6.0 for *spiegel*, and 7 to $7\frac{1}{2}$ for ferro-manganese, estimating manganese by difference. Thus:—

Spiegeleisen.

Iron	84.25 per cent.
Carbon, silicon, &c. ..	6.00 "
Manganese (by diff.) ..	19.75 "
<hr/>	
	100.00

Arsenic.

Should arsenic be contained in the iron or steel, it will be precipitated along with the copper as sulphide, upon passing a current of sulphuretted hydrogen gas through a solution of the metal as previously described. For the separation of the two metals advantage is taken of the fact that sulphide of arsenic is soluble in hydrogen potassium sulphide (KHS), while copper sulphide is not.

The precipitate of mixed sulphides is digested with a moderate excess of hydrogen potassium sulphide, the insoluble copper sulphide collected on a filter, dissolved in nitro-hydrochloric, and the copper precipitated as oxide by means of caustic soda as previously described. To the filtrate remaining after treatment with KHS, add a small quantity of hydrochloric acid, collect the resulting precipitate of sulphide of arsenic on a filter, treat with carbon disulphide to remove free sulphur, rinse the precipitate into a beaker, and dissolve in nitro-hydrochloric acid. Filter, if necessary, and precipitate the arsenic as magnesium-ammonium arseniate, by adding to the cold filtrate a small quantity of magnesia mixture, and then a large excess of ammonia. Allow the solution to stand for twenty-four hours, collect the precipitate on a weighed filter, wash with ammonia water until a drop of the washings, after acidification, with nitric acid, gives only a slight opalescence with silver nitrate. Dry the filter and contents in a water oven, and convert the magnesium-ammonium-arseniate, contained in a weighed porcelain crucible, by ignition, at a red heat, into $Mg_2As_2O_7$, which contains 48.30 per cent of arsenic.

To prepare the magnesia mixture, dissolve 83 grms. of magnesia sulphate in water, add 5 c.c. of hydrochloric acid and 83 grms. of barium chloride dissolved in water. Filter a small portion of the solution, add a little sulphuric acid, and if a precipitate is formed add a further quantity of magnesia sulphate to the original solution. Filter, concentrate the filtrate, cool, add 165 grms. of ammonium chloride, together with 260 c.c. of ammonia, dilute to a litre. Allow to stand for a few days, and decant from any precipitate formed.

It is advisable to test all steels for this element, and it must be borne in mind that arsenic acid is precipitated together with phosphoric; the former must, therefore, be eliminated previous to the determination of phosphorus in steel, iron, &c.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 1st, 1893.

Dr. ARMSTRONG, President, in the Chair.

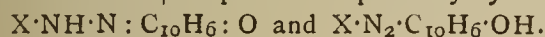
MESSRS. T. L. BAKER, J. Addyman Gardner, James Mason, Robt. G. Grimwood, and Reginald B. Brown were formally admitted Fellows of the Society.

The certificate of Frank Browne, Government Civil Hospital, Hong Kong, was read for the first time.

Of the following papers those marked * were read:—

*25 "Azo-compounds of the Ortho series." By R. MELDOLA, E. M. HAWKINS, and F. B. BURLS.

The constitution of the orthazo compounds is still an unsolved problem owing to the contradictory results obtained by different investigators using different methods. The evidence in some cases points to the hydrazone formula and in others to the azo-formula, represented in the case of the azo β -naphthols respectively by—



The compounds may really be isodynamic; but their acetyl and benzoyl, &c., derivatives, which were first investigated by one of the authors and G. T. Morgan (*C. S. Trans.*, 1889, 114), can hardly be thus regarded. The best evidence in favour of the hydrazone formula was furnished by Goldschmidt and Brubacher (*Ber.*, 1891, 2300), who obtained acetanilide and benzanilide by reducing the acetyl and benzoyl derivatives by means of zinc dust and acetic acid in alcoholic solution: these products are not obtained when stannous chloride is used as the reducing agent, a fact which was made known in 1889 in the paper referred to, and which has been confirmed in the present investigation.

In repeating Goldschmidt and Brubacher's work with the acetyl derivatives of ortho- and para-tolueneazo- β -naphthol, the authors have found that acetamido- β -naphthol is also one of the products of reduction, and in the case of a number of other acetyl derivatives this compound is found to be a normal product of reduction. Thus, in the case of an acetyl derivative of the form $X \cdot N_2 \cdot C_{10}H_6 \cdot OC_2H_3O$ or $X \cdot N(C_2H_3O) \cdot N : C_{10}H_6 : O$, four products are always obtained when zinc dust and acetic acid is the reducing agent, viz.:— $X \cdot NH \cdot C_2H_3O$, $C_{10}H_6(NH \cdot C_2H_3O) \cdot OH$, $X \cdot NH_2$, and $C_{10}H_6 \cdot NH_2 \cdot OH$. The quantity of acetamido- β -naphthol is very small in the case of the acetyl derivative of benzeneazo- β -naphthol, a fact which accounts for this product having been overlooked by Goldschmidt and Brubacher. As the number of methyl groups in X is increased, the quantity of acetamido- β -naphthol increases, the acetyl derivative of pseudo-cumeneazo- β -naphthol giving about 9.2 per cent of this product when reduced by zinc dust and acetic acid in the manner described.

The following azo-compounds and their acetyl derivatives have been isolated and characterised in the course of the investigation:—

<i>p</i> -Tolueneazo- β -naphthol (acetyl derivative)	Red prisms, m. p. 99°.
<i>p</i> -Chlorobenzeneazo- β -naphthol (acetyl derivative)	Flat needles or leaflets, red, m. p. 133°.
Pseudocumeneazo- β -naphthol	Bronzy prisms or bright scarlet needles, m. p. 163° to 164°.

Other acetyl derivatives have been prepared, but used immediately for reduction for reasons explained in the paper. The acetyl derivative of benzeneazo- β -naphthol has been reduced under various conditions, and is always found to give a small quantity of acetamido- β -naphthol except when stannous chloride is used, when the chief

product appears to be either a naphthylphenyl or a naphthylphenylamine derivative. The latter will be made the subject of a special investigation. Even when zinc dust and chlorhydric acid were used as reducing agents, acetamido- β -naphthol was obtained, but the quantity of acetanilide is in this case insignificant, the chief products being amido- β -naphthol and aniline.

The authors conclude that the formation of acetamido- β -naphthol on reduction is destructive of Goldschmidt and Brubacher's evidence in favour of the hydrazone formula for the ortho-azo compounds. The simultaneous formation of acetanilide, acetoluide, &c., and acetamido- β -naphthol cannot be explained by either azo- or hydr-azone formula alone; but if it be assumed that an intermediate product of the nature of an anhydro compound is formed, the production of these compounds is accounted for. It is shown in the paper that the same anhydro compound would be produced whether the acetyl group were attached to nitrogen or oxygen in the original compound, so that the question of the constitution of the ortho-azo compounds still remains an open one. Further experiments on the reduction of the acetyl and benzoyl derivatives of other ortho-azo compounds are in progress.

*26. "The Production of a Fluorescein from Camphoric Anhydride." By J. NORMAN COLLIE, Ph.D., F.R.S.E.

Last year the author proposed a formula for camphoric acid of the succinic type (*Ber.*, xxv., 1116). Up to that date no fluorescein had been prepared from camphoric anhydride, and it had even been stated that this anhydride did not form such a compound (*J. E. Marsh, C. S. Trans.*, 1891, 651); it therefore seemed necessary to institute further experiments to obtain an explanation of this apparently anomalous behaviour of camphoric anhydride. The author finds that under suitable conditions camphoric anhydride is without difficulty converted into a fluorescein, the best results being obtained by heating one molecular proportion of the anhydride with two molecular proportions of resorcinol to about 180° C., with a relatively small amount of zinc chloride.

The resulting fluorescein, ($C_{22}H_{22}O_5$), is a reddish-brown powder, which, when dry, has a greenish lustre. It dissolves in alkalis, affording a pink-coloured solution, and exhibits in dilute aqueous solutions a beautiful green fluorescence.

When sulphuric acid is employed in its preparation, the yield of fluorescein is small, the chief product being a brown compound which dyes cotton mordanted with alumina a pink colour.

The author finds that isopropylglutaric anhydride also furnishes a fluorescein, so that the production of a fluorescein from camphoric acid does not afford evidence which can be made use of in deciding whether the acid is a compound of the succinic or of the glutaric type.

*27. "Researches on the Terpenes. III. The Action of Phosphorus Pentachloride on Camphene." By J. E. MARSH and J. A. GARDNER.

The authors describe the results of the further study of the action of phosphorus pentachloride on camphene. When these substances are allowed to interact without heat being applied, a mixture of camphene hydrochloride and a chlorophosphonic derivative of the formula $C_{10}H_{15}PCl_4$ is obtained. On treatment with water, the latter compound is converted into a mixture of acids which, together with the camphene hydrochloride, forms a syrupy mass, from which the acids are separated by fractionally extracting with a solution of sodium carbonate. After further purification by means of suitable solvents, two well-characterised isomeric camphenephosphonic acids of the formula $C_{10}H_{15}PO_3H_2$ were obtained.

a-Camphenephosphonic acid, crystallised from dilute alcohol, has a composition represented by the formula $2C_{10}H_{15}PO_3H_2 + H_2O$. It is characterised by its insolubility in ether and ready solubility in chloroform; when heated at 100° it loses the elements of two molecules of

water. The anhydrous acid melts at 184° . The acid is monobasic. The sodium salt crystallises from water or alcohol; the barium salt forms an almost insoluble crystalline precipitate.

β -Camphenephosphonic acid, crystallised from dilute alcohol, has the composition $C_{10}H_{15}PO_3H_2$. It does not lose weight when heated during several hours at 100° , but on prolonged heating it turns brown, melts, and loses weight. It is readily soluble in ether, but insoluble in chloroform; it melts at 170° . The acid is monobasic. The sodium and ammonium salts have been prepared.

The α - and β -acids further differ in rotatory power. When prepared from camphene having a rotatory power of -60° , the specific rotatory power of the α -acid was $[\alpha]_D = -119^{\circ}$, and that of the β -acid -71° .

When the mixture of phosphorus pentachloride and camphene is heated, a crystalline compound of the formula $C_{10}H_{14}PCl_3$ is obtained, which has been previously described (*C. S. Trans.*, 1891, 652). When subjected to the action of a solution of sodium carbonate, this compound yields a sodium salt of the formula $C_{10}H_{14}ClPO_2NaH + 5H_2O$. The corresponding barium salt is soluble in water, and crystallises with three molecular proportions of water. The acid is an oil. On oxidation by potassium permanganate in alkaline solution it is converted into the corresponding chlorocamphenephosphonic acid, $C_{10}H_{14}PO_3H_2$. This may be crystallised from benzene; it melts at 178° , undergoing decomposition. When a mixture of camphene with a larger excess of phosphorus pentachloride is heated, and the product is hydrolysed, the same chlorocamphenephosphonic acid is obtained, together with an isomeric acid. The sodium salts of all these phosphonic acids are acted on by bromine, the phosphonic group appearing in solution as sodium phosphate, brominated derivatives of camphene being produced, which are under investigation. On oxidation by nitric acid, chlorocamphenephosphonic acid yields camphonic acid. On fusing chlorocamphenephosphonic acid with potash, a very small quantity of a crystalline volatile substance was obtained.

*28. "The Composition of a Specimen of Jute Fibre produced in England." By ANDREW PEARS, Jun.

The author succeeded in securing a normal growth of the jute plant (*Corchorus capsularis*) in a "hothouse" of average temperature, $65^{\circ} F$. The stems, 5 feet in length and branched, were cut down after maturation of the seed, which has since been germinated for growth during the current year. The stem-fibre was separated after retting in tepid water, and was exhaustively investigated. It showed the characteristic behaviour of lignocelluloses, but with important variations in degree; the most marked difference observed was in ultimate composition, the carbon percentage being only 43 as against 46–47 in the normal fibre. From the results, given in full in the paper, it is shown that the factors of lignification induce variation in chemical composition, within wide limits, at the same time that the general constitutional type is preserved. Lignification may, in fact, be regarded as a gradual passage from "saturated" to "unsaturated" compounds, and as the result of the splitting off of water and carbon condensation, the specimen in question representing the earlier phases of such transition or evolution.

29. "Note on the Combination of Dry Gases." By W. RAMSAY, F.R.S.

Mr. H. Brereton Baker has stated in his recent note that when dry ammonia is mixed with dry hydrogen chloride, these gases do not combine to form ammonium chloride; I would therefore call attention to a statement to the same effect by Dr. Sydney Young and myself in a paper on "Evaporation and Dissociation," published in the *Phil. Trans.*, 1886, Part I., p. 89. After describing the behaviour of ammonium chloride at 280° in a modified Hofmann's vapour-density tube, we state:—"When the tube cooled, a permanent gas remained, which exerted a

pressure of 18.3 m.m. As a very long time was allowed so as to make certain of no further rise (of pressure) when the ammonium chloride was heated, the presence of this gas cannot be accounted for by a gradual decomposition of the ammonia, for we have shown (*J. Chem. Soc.*, 1884, 88) that ammonia begins to decompose only at 500° , even when hydrochloric acid is absent. It might, however, to some extent be due to the action of hydrochloric acid on mercury. On inclining the tube, this gas formed a bubble of considerable size at the top. Water was introduced, and almost complete absorption occurred. It appears certain, then, that gaseous hydrogen chloride and ammonia, when perfectly dry, combine very slowly."

These experiments were made in order to measure the vapour pressure of ammonium chloride; hence there was always a large excess of solid chloride present. It appears, therefore, that even in presence of the associated solid compound, the gaseous constituents may remain in presence of each other without combining.

I was not so successful as Mr. Baker has been in preventing the combination of nitric oxide and oxygen. Even after a bulb of nitric oxide containing several grms. of phosphoric anhydride—itsself contained in a bulb of oxygen in which there was a considerable quantity of the anhydride—had been left during three months, on breaking the thin-walled inner bulb, a red colour was at once seen. I cannot but conclude that some substance other than water vapour may also have the power of effecting such combination; unless, indeed, it be contended that such a lengthened exposure to phosphoric anhydride does not completely dry the gases.

30. "Ortho-, Para-, and Peri-disulphonic Derivatives of Naphthalene." By HENRY E. ARMSTRONG and W. P. WYNNE.

In a previous communication, dealing with the results of the examination of a large number of disulphonic acids (*Proc. C. S.*, 1890, 133), attention was drawn to the "invincible objection" of two sulphonic radicles to remain in either contiguous or para- or peri-positions" relatively to one another when disulphonic acids are formed by the action of sulphuric acid either on naphthalene or on the chloro-, amido-, or hydroxy-naphthalenes. Further investigation has failed to supply a single exception to this rule, and it is noteworthy that of the known disulphonic acids only two—the No. II. α -naphthylamine-disulphonic acid of Dahl and Co.'s German Patent No. 41957 (*loc. cit.*, p. 125), and the minor product of the sulphonation of potassium 2:3'-chloronaphthalenesulphonate (*loc. cit.*, p. 132)—contain the two sulphonic radicles relatively in the positions 1:2', the favoured positions being 1:4', 2:4', 2:2', and 2:3', the position 1:3 being taken up only in the case of sulphonation products of certain β -chloro- and β -amido-naphthalenesulphonic acids. Moreover, while the number of naphthalene-disulphonic acids obtainable, either by the sulphonation of naphthalene or by eliminating the NH_2 radicle from naphthylaminedisulphonic acids, amounts to six, it is very significant that only two naphthylaminetrisulphonic acids—the 1:3:2'- and the 1:3:3'-derivatives—can be obtained by sulphonating naphthalene, and that the only trisulphonic acids obtained by sulphonating the naphthols and naphthylamines contain their sulphonic radicles relatively in one or other of these positions.

While preparing the final account of our seven years' investigations, we endeavoured in various ways to prepare the missing acids containing the sulphonic radicles in the positions which are avoided in all products of direct sulphonation, so that their behaviour towards sulphonating agents might be studied in order that the explanation of this remarkable law of substitution might be given. While engaged in these experiments, we learnt with great satisfaction from Dr. C. Duisberg that a process had been devised in the laboratory of the *Faberrfabriken vormals F. Bayer and Co.*, of Elberfeld,

which had enabled them to prepare all the acids we were in search of, and with that courtesy which is characteristic of German chemical manufacturers Dr. Duisberg at once communicated their method to us, so that we might proceed to study the various acids from the scientific side.

The process consists in displacing the amido-group in a naphthylamine derivative by SH and oxidising the resulting thio-derivative by means of alkaline permanganate; the thihydride is prepared by Leuckart's method (*J. Pr. Chem.*, [2], xli., 218) by submitting the diazo-compound prepared from the amine to treatment with potassium xanthate and hydrolysing the resulting xanthate. The thihydride thus formed being unstable in presence of oxygen, the corresponding disulphide is usually obtained. The process is described in the German Patent Anmeldung F. 6099, Cl. 22, of the Farbenfabriken vorm. Friedr. Bayer and Co., Elberfeld, in which an account is given of three new disulphonic, seven new tri-sulphonic, and two tetrasulphonic acids of naphthalene. With no more information before us than is afforded by the specification, we have been able without the slightest difficulty to prepare the various acids, and we have nothing to add to the admirable description given in the specification—a striking illustration of the character of the German chemical patent literature of the day.

In the present note only three new disulphonic and one new trisulphonic acid are referred to; the remaining acids will be described in a later communication. On treatment with phosphorous pentachloride, the 1:1'- and 1:2-acids yield products which apparently are the corresponding anhydrides. This behaviour is of interest as an extension of the observations made in V. Meyer's laboratory on the formation of anhydrides of disulphonic acids of thiophen. It is remarkable that the R-acid, in which there are two contiguous β -sulphonic groups, has not been found to yield an anhydride.

In the first instance, we availed ourselves of the method to prepare from the (Badische) 1:2'- β -naphthylamine-sulphonic acid the 1:2'-naphthalenedisulphonic acid previously discovered by us (*Proc. Chem. Soc.*, 1890, 125). The product is identical with that obtained from Dahl's No. II. α -naphthylaminedisulphonic acid, and thus an independent proof is afforded of the somewhat remarkable constitution which we have assigned to this acid.

1:1'-Naphthalenedisulphonic acid was prepared from the Schöllkopf 1:1'- α -naphthylaminesulphonic acid kindly placed at our disposal by the Actiengesellschaft für Anilinfabrikation, Berlin. The corresponding potassium naphthalenesulphidesulphonate, $(C_{10}H_6S \cdot SO_2K)_2 + H_2O$, crystallises in very small pale yellow scales, sparingly soluble in cold water. Potassium 1:1'-naphthalene disulphonate, $C_{10}H_6(SO_3K)_2 + H_2O$, crystallises in well-defined, four-sided scales sparingly soluble in hot water; what appears to be the corresponding anhydride crystallises in small, rhomboidal, probably monosymmetric plates, melting at 227° , which are sparingly soluble in hot benzene, more soluble in hot xylene and acetic acid.

1:2-Naphthalenedisulphonic acid was obtained from the Landshoff and Meyer 1:2- α -naphthylaminesulphonic acid. The corresponding potassium naphthalenesulphidesulphonate, $(C_{10}H_6S \cdot SO_3K)_2 + 4H_2O$, crystallises in pale yellow granules consisting of microscopic prisms sparingly soluble in cold water. Potassium 1:2-naphthalenedisulphonate, $C_{10}H_6(SO_3K)_2 + \frac{3}{2}H_2O$, crystallises from water in very soluble prismatic tables; what appears to be the corresponding anhydride crystallises from benzene, in which it is tolerably soluble, in elongated striated prisms melting at 198° .

1:4-Naphthalenedisulphonic acid was prepared from naphthionic acid. The corresponding potassium naphthalenesulphidesulphonate, $(C_{10}H_6S \cdot SO_3K)_2 + 2H_2O$, crystallises from water in easily soluble, pale yellow, microcrystalline granules. Potassium 1:4-naphthalene-disulphonate, $C_{10}H_6(SO_3K)_2 + 1\frac{1}{2}H_2O$, crystallises from water in small readily soluble needles; the corresponding

chloride, $C_{10}H_6(SO_2Cl)_2$, crystallises from benzene, in which it is readily soluble, in four-sided, monosymmetric plates showing an optic axis just beyond the edge of the microscope field; this melts at 160° .

2:2':3'-Naphthalenetrisulphonic acid was obtained from 2:2':3- β -naphthylaminedisulphonic acid (amido-R-acid). The corresponding potassium naphthalenesulphidesulphonate, $[C_{10}H_5S(SO_3K)_2]_2 + 5H_2O$, crystallises from water in finely striated prismatic forms having a beautiful velvet-like appearance. Potassium 2:2':3'-naphthalenetrisulphonate, $C_{10}H_5(SO_3K)_3 + 3H_2O$, crystallises from water in small, microcrystalline, spherical aggregates; the corresponding chloride, $C_{10}H_5(SO_2Cl)_3$, crystallises from benzene, in which it is tolerably soluble, in long, flat, probably monosymmetric plates showing longitudinal striations, melting at 200° .

The method of substituting the SO_3H radicle for NH_2 has been extended to the chloro- β -naphthylamine-sulphonic acids, and in particular to the 1:2:2'- or "No. III." acid, with the object of comparing the product with the α -chloronaphthalene-2:2'-disulphonic acid obtained from Alén's α -nitronaphthalene-2:2'-disulphonic chloride, to which Cleve attributes a like constitution (*Ber.*, xxv., 2490). We take this opportunity of stating that further investigation has shown that, contrary to our previously expressed view (*cf. Proc. Chem. Soc.*, 1890, 135), the No. 2 and No. 3 acids have an independent origin.

By the discovery of the disulphonic acids here described, we are now placed in possession of nine of the ten possible acids. We have previously characterised the ten possible dichloronaphthalenes and the two homonuclear trichloronaphthalenes (*Proc. Chem. Soc.*, 1890, 76, 77); we have now all but completed the study of the remaining twelve trichloronaphthalenes, having converted them into sulphonic acids, &c., in order that it may be possible to characterise them beyond question. So soon as the few remaining comparisons are completed, a detailed account of the investigation will be submitted.

Experiments are being carried out in the Central Institution laboratory by one of us with the object of determining, by means of the xanthate method, whether in the case of other hydrocarbons orthodisulphonic acids can be obtained which can exist in presence of sulphonating agents—the statements on record being far from satisfactory, and in some cases contradictory.

31. "Supplementary Notes on Madder Colouring-Matters." By E. SCHUNCK, Ph.D., F.R.S., and L. MARCHLEWSKI.

Many years ago (*Phil. Trans.*, 1853, 72) one of the authors described under the name of rubiadin a yellow colouring-matter obtained from madder. It is now shown that madder contains a glucoside of this substance, the preparation and properties of which are described. The glucoside crystallises in yellow needles melting at about 270° . On acetylation by Liebermann's method, it yields a pentacetyl derivative. On treatment with baryta-water it yields a dark red lake, one hydrogen atom being displaced by barium. On hydrolysis, it is converted into rubiadin and ordinary dextrose,—



Rubiadin crystallises in lustrous yellow needles melting at 290° . It very closely resembles purpuroxanthin, and is probably the corresponding derivative of methylanthracene.

32. "The Constitution of Rubiadin Glucoside and of Rubiadin." By L. MARCHLEWSKI.

It is pointed out that of the five hydroxyl groups in rubiadin, one is phenolic, inasmuch as the glucoside yields dark red coloured mono-metallic derivatives; further, it is contended that probably glucose always exists in glucosides in the form of an anhydride of a hepta-hydric alcohol; a formula is assigned to the glucoside based on these arguments.

Assuming that rubiadin is derived from the same (8) methylanthracene as emodin, &c., it is pointed out that there are still three possible formulæ if rubiadin be regarded as a meta-dihydroxyanthraquinone—one homo- and two hetero-nuclear.

By heating a mixture of symmetrical metadihydroxybenzoic acid, paramethylbenzoic acid, and sulphuric acid at 110° , the author has obtained a substance of the same composition and closely resembling rubiadin, but melting at 267° .

PHYSICAL SOCIETY.

Ordinary Meeting, June 9th, 1893.

Prof. J. PERRY, F.R.S., Vice-President, in the Chair.

Prof. A. JAMIESON, Prof. H. Stroud, and Mr. J. Wade were elected Members of the Society.

Mr. A. P. TROTTER read a paper on "*A New Photometer*." The author has modified his "*Illumination Photometer*," described *Proc. I.C.E.*, vol. cx., Paper No. 2619, so as to adapt it to the measurement of candle-power. The principle employed is to view a screen illuminated by one source through an aperture in a second screen illuminated by the other light, the aperture becoming invisible when the illuminations are equal. After using perforations of various patterns, a series of narrow slots cut in thin paper were found to give the best results. The plain screen is mounted behind the slotted one in a box sliding on the photometer bench, and they are arranged so that the light falls on them at equal angles. The screens are viewed, from a distance of 6 or 7 feet, through an opening in the front of the box, cords being provided for producing the traversing motion. Two "sights" set respectively at the middle of the length of the plain screen, and on the lower edge of the front opening, serve to show when the middle of the band of equal illumination is vertically above the pointer on the carriage. The photometer is found to be particularly valuable when it is desired to determine the maximum power of a variable source. When lights of different colour are being compared, say a gas-flame and an arc, one end of the screen shows blue strips on a yellow ground, and the other end yellow strips on a blue ground; at the centre the colours seem to blend. To facilitate the comparison of such lights, Mr. Crompton, who has been working at the subject simultaneously with the author, uses one screen tinted pale yellow and the other pale blue. Details of construction of the new photometer are given in the paper, and the accuracy attainable when comparing two equal lights of about eight candles is stated to be about 1 per cent.

Prof. S. P. THOMPSON, D.Sc., F.R.S., read "*Some Notes on Photometry*."

The first note relates to "*The Use of Two Overlapping Screens as an Isophotal*," and describes the evolution of the Thompson-Starling photometer. In this instrument a prismatic block, with apex upwards, rests crosswise on the photometer bench, and the inclined sides are respectively illuminated by the two sources to be compared. In testing differently coloured lights, coloured stuffs were placed over the surfaces of the edge. In some cases notched and overlapping cards were used to form the overlapping surfaces. An inclination of about 70° between the two surfaces was found convenient.

The second note refers to the "*Periodic Principle in Photometry*," and in it the author discusses various methods which have been, or may be, used for producing small difference of decreasing amount between the two sides of a photometer screen. By employing a device of this kind much greater accuracy of adjustment is possible. In one form of vibration photometer worked out by the author, the paraffin blocks of a Jolly's photometer are mounted at one end of a spring, the other end being fixed to the carriage. The act of moving the carriage

starts the blocks vibrating, thus producing the desired variations.

In a third note the question of using "*The Electric Arc as a Standard of Light*" is dealt with. Since 1878 the positive crater has been used as a standard of whiteness, and last year both the author and Mr. Swinburne suggested that a given area of crater might be used as a standard of light. This proposal has since been carried out by M. Blondel. Since the intrinsic brilliancy of the crater is high, it necessitates very small apertures, or else the use of standards of large candle-power. Advantages of using powerful standards are pointed out in the paper. With a circular hole 1 m.m. in diameter a standard of about fifty-five candles could be obtained; with such a source benches longer than usual would be preferable. At the end of the note the errors which may be introduced by using, as an arc standard, a hole in a plate of sensible thickness, when viewed obliquely, are investigated, as well as those due to inaccuracy of setting the plane of a hole made in foil perpendicular to the photometer bench.

Major-General FESTING, in opening the discussion on both papers, said reflection from the sides of the hole in a thick plate would tend to lessen the error calculated by Prof. Thompson. The ordinary impurities in carbon were not likely to alter the brilliancy of the crater. Capt. Abney and himself had no reason to distrust its constancy. Both the vibrating photometer and Mr. Trotter's arrangement would be very useful.

Dr. SUMPNER said his photometric experience had been obtained with the Bunsen, Jolly, and Lummer-Brodhun types. With the two former the inaccuracy arising from uncertainty of adjustment was about $\frac{1}{2}$ per cent.; changes of about 0.4 per cent (average) resulted from reversing the screens. The Lummer-Brodhun instrument (which he described) was better than either of the other two, the average error being about $\frac{1}{4}$ per cent.

Mr. FRANK WRIGHT thought scientific men gave too little attention to the question of light standards. Photometers could be relied on much more than any standard at present in use. The Methven screen was the most practical standard yet devised, but in his opinion no gaseous flame could be a real standard on account of the influence of the surrounding atmosphere.

Prof. AYRTON saw difficulties in using long benches as suggested by Dr. Thompson, on account of the serious atmospheric absorption which occurs with light from arcs. Decreasing the intensity by dispersion or otherwise was preferable. In some tests on glow lamps now being carried on at the Central Institution, a Bernstein lamp used as a standard was mounted on a spring and vibrated.

Mr. MEDLEY showed the vibrating standard referred to by Prof. Ayrton, and gave a series of numbers showing that with this device in conjunction with the Lummer-Brodhun photometer accuracies of about $\frac{1}{4}$ per cent were obtainable.

Mr. SWINBURNE thought Mr. Trotter's arrangement was better than the "wobbling" photometer. As to the best length of bench he was inclined to think the shorter the better, provided its dimensions were large compared with those of the standard light. He concurred with Mr. Wright in his remarks about the desirability of obtaining a better standard. Speaking of the arc as a standard he said that only impurities less volatile than carbon would influence the brightness. An important factor was the emissivity of the carbon, which might not be constant.

Mr. BLAKESLEY thought the accuracy obtainable with Mr. Trotter's photometer had been underrated, and pointed out that by using quadrant-shaped screens intersecting orthogonally on the axis of the photometer instead of straight ones, the width of the neutral band could be greatly diminished.

Mr. TROTTER, referring to Dr. Thompson's paper, said he had found considerable difficulty in making pin-holes suitable for arc standards. It was not an easy matter to accurately measure the hole when made. In photometric

measurements he had found it very important to reverse his screens. Curved screens, as suggested by Mr. Blakesley, had been tried, but with little advantage. They also destroyed the approximate direct-reading property of the photometer. The subject of changing the length of a bench and its effect on the gradient of illumination was discussed. With short benches one had to guard against the departure from the inverse-square law, due to appreciable size of the standard. Recent experiments had shown that the light given out by 1 square m.m. of crater surface differed considerably from 70 candles.

A paper on "*The Magnetic Field close to Surface of a Wire Conveying an Electric Current*," by Prof. G. M. Minchin, M.A., was taken as read. In this paper the author applies the solution he gave in March last for the conical angle subtended by a circle at any point in space to determine the negative potential at a point near the surface of a ring of wire of circular cross section. The shapes of the lines of force near the surface, for several laws of current distribution across the section, have also been worked out.

CORRESPONDENCE.

ON THE ANALYSIS OF PIGMENTS WHEN GROUND IN OIL.

To the Editor of the Chemical News.

SIR,—Referring to Mr. J. B. Hannay's paper under the above title in the *CHEMICAL NEWS*, lxvii., 268, the method usually adopted for the extraction of oil from white-lead is to treat from 30 to 50 grms. in a Soxhlet apparatus with methylated ether (absolute), removing the white-lead after, say, four hours, drying and grinding, and re-extracting with ether until on testing no further oil is obtained.

If the greater part of the ether be removed by evaporation, and the residue, after filtration through several Swedish filters, tested by passing sulphuretted hydrogen, a distinct trace of lead sulphide is always obtained. Even adopting the process of extraction suggested by Mr. Hannay (which would be impracticable in commercial work), on evaporating down the large volume of ether used to a small bulk, a trace of lead is found. Thus in an experiment with 50 grms. of Stack white-lead and 5 litres of ether, a distinct trace of lead was obtained, and also a trace of oil on dissolving the 50 grms. in nitric acid.

I fear that it will be a very long time before Mr. Hannay succeeds in educating the "ignorant tradesman" to use his so-called white-lead (sulphate of lead) in preference to that made by the Stack process.—I am, &c.,

R. H. HARLAND.

37, Lombard Street, E.C.,
June 15, 1893.

The Odoriferous Power in the Fatty Series.—Jacques Passy.—In an odoriferous substance the author distinguishes three properties,—the power, the intensity, and the quality. The power is the inverse of the minimum perceptible. The minimum perceptible of camphor being 5 and that of vanilla 0.005 in millionths of a gm., the odoriferous power of vanilla is 100 times that of camphor. Of two odours, the more intense is that which masks the other. The following Table gives the substances in the order of their power, which is almost the inverse order of their intensity:—Camphor, 5; ether, 1; citral, 0.5 to 0.1; piperonal, 0.1 to 0.05; coumarine, 0.05 to 0.01; vanilline, 0.005 to 0.0005. The quality is that which distinguishes one odour from another.—*Bull. de la Soc. Chim. de Paris*, ix.—x., No. 11.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 22, May 29, 1893.

The Volatilisation of Silica and Zirconia, and the Reduction of these Compounds by Carbon.—Henri Moissan.—This paper will be inserted in full.

Preparation in the Electric Furnace of the Refractory Metals, Tungsten, Molybdenum, and Vanadium.—Henri Moissan.—This paper also will be inserted in full.

The Preparation of Zirconium and Thorium.—L. Troost.—This paper will be inserted in full.

Observations on the Volatilisation of Silica, with Reference to the Communication of M. Moissan.—P. Schützenberger.—I have heard with the warmest interest the important communication of M. Moissan. The fact which he has distinctly established—of the volatility of silica at a very high temperature—supplies the explanation of phenomena which I observed a long time ago in the course of a research executed in concert with M. Colson, phenomena which in my opinion ought to incite to further researches. We observed:—1. That pure silica placed in small crucible of retort coke enclosed in a larger crucible lined with lamp-black and heated for some hours in a good blast furnace, loses a notable quantity of its weight. 2. That platinum gains weight, becomes fusible, and takes up silicon, even if placed in a covered crucible of coke, plunged in a thick "brask" of lamp-black, and heated to whiteness for two hours. This effect is not produced if the lamp-black is replaced by a mixture of black and of rutile in powder, but if we introduce silica into the crucible of coke containing the platinum and separating the two substances by a plate of coke, the platinum becomes loaded with silicon and melts even in a titaniferous "brask." Silicon substituted for silica has no action, and does not seem to be volatile. All these facts are easily intelligible if we admit, as M. Moissan has proved, the volatility of silica.

Action of Acetic Anhydride upon Linalol; Transformation into Geraniol.—G. Bouchardat.—According to the experiments of the author, linalol or licaléol modified by etherification appears identical with geraniol. Consequently the aldehyd derived from linalol is identical with geraniol, of a citron odour, $d_0 = 0.898$.

General Method for the Analysis of Butters.—Raoul Brullé.—This paper will be inserted in full.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. ix. and x., No. 9.

Monobromgallic Acid and its Derivatives.—Alex. Biétrex.—This acid contains three molecules of crystal line water. The author has obtained and examined the ammonium lead, monobromogallates, and the triacetyl-monobromgallic acid.

New Process for Obtaining Oxyhæmoglobine by means of Oxyhæmatine and an Albumenoid Substance.—H. Bertin-Sans and J. Moitessier.—The authors' process renders it possible to obtain, extemporaneously by means of solutions of oxyhæmatine and of albumenoid matter, very concentrated solutions of a compound which presents very distinctly the appearance and the spectral reactions of hæmoglobine, and containing no impurities except a slight excess of the albumenoid matter.

The Féry Refractometer.—This paper requires the accompanying illustrations.

Determination of Manganese in its Ores and its Alloys.—Ferdinand Jean.—This paper will be inserted in full.

Analysis of Impure Galenas and New Method of Determining Copper and Zinc.—Ferdinand Jean.—This paper also will be inserted in full.

Volumetric Determination of Copper, Iron, Antimony, and Zinc in Powder.—Ferdinand Jean.—The substance of this paper has been already noticed.

Use of Superphosphates.—Jules Joffre.—Already inserted.

Manufacture of Extracts of Dye-woods.—A. and P. Buisine.—This article consists of extracts from a memoir on the subject which appeared in 1891 in the *Bulletin de la Société Industrielle de Mulhouse*.

Concentration of Sulphuric Acid.—A. and P. Buisine.—This bulky paper requires the ten accompanying cuts.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Photographic, 8.

WEDNESDAY, 28th.—Society of Arts, 4. (Anniversary).
British Astronomical Association, 3.

FLETCHER'S THERMO-HYDROMETER.



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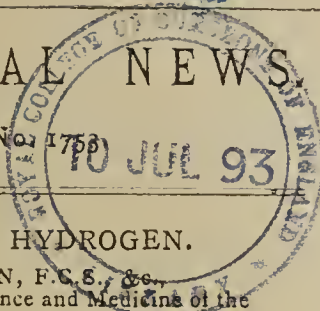
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THE CHEMICAL NEWS.

VOL. LXVII., No. 1758



VEGETATION IN HYDROGEN.

By Dr. T. L. PHIPSON, F.C.S., &c.,
Graduate of the Faculties of Science and Medicine of the
University of Brussels.

IN a recent paper, in which I made known the views of the late Prof. Koene on the constitution of the atmosphere at remote periods of the earth's history,* I promised to continue my experiments with carbonic acid.

From Koene's view that no free oxygen could have existed in the atmosphere when life first appeared on the globe, because we find oxidisable substances in the primitive rocks, and that the original atmosphere of the globe at that period was formed exclusively of carbonic acid and nitrogen, it follows, as I hinted before, that oxygen—the essential element of modern life—must have been derived from the vital functions of inferior plants, from the *protocista*, or first created living beings, having the power of separating it from its compounds, carbonic acid and water.

It therefore became interesting to ascertain to what extent our modern plants can vegetate in carbonic acid, and to extend this inquiry to hydrogen and nitrogen.

I had noticed, many years ago, that certain plants (willow, lilac, &c.) did not thrive in an excess of carbonic acid, and concluded that the diminished quantity of this gas now existing in our air was the condition which suited them best. In experiments carried out this year, I have placed various other plants (*Poa*, *Myosotis*, *Antirrhinum*, and *Convolvulus*) in an atmosphere composed of pure carbonic acid, and in an atmosphere composed of air with about 100 times more of this gas than exists in our atmosphere. All other conditions of vegetation were normal: there was ample water, mineral elements, and an appropriate temperature (59° to 70° F.) during the course of the observations.

I found that my plants could exist for many days, or even weeks, in an atmosphere of pure carbonic acid, but they did not thrive; cell formation became slower and slower. In an atmosphere containing so much carbonic acid that an animal exposed to it would perish in a few minutes, plants lived for many weeks and appeared healthy. In an atmosphere containing 100 times as much carbonic acid as in the natural state of the air, plants flourished remarkably well for the whole time the experiment lasted (a month to six weeks).

It is therefore highly probable, as Koene held, that in former geological periods (the coal period, for instance) there existed plants which could live in an atmosphere excessively rich in carbonic acid, and that the quantity of that gas in the air has really decreased from that time to this, the loss being represented by the vast deposits of peat, lignite, coal, and anthracite found in the strata of the earth.

My next experiments were made with pure hydrogen gas, to see what would happen when plants are placed in an atmosphere consisting of nothing but hydrogen (a gas which many look upon as the vapour of a metal); all other conditions being normal, namely, water charged with carbonic acid and containing the necessary mineral elements.

The plants I placed in an atmosphere of pure hydrogen were *Convolvulus arvensis* (a plant which is very hardy and convenient for observations of this kind), and *Antirrhinum majus*.

For the first few days nothing peculiar was noticed. From May 27 to the end of the month, a slight bleaching of the leaves only was apparent, but by June 3 a singular phenomenon occurred: *the volume of gas began to diminish*, and in the course of a month the atmosphere of hydrogen in which vegetated the *Convolvulus* was absorbed to the extent of about 80 per cent. The residue, 20 per cent, was not hydrogen; so it may safely be said that *the whole of the hydrogen had disappeared*, the plant remaining perfectly healthy.

I explain this by assuming that the nascent oxygen emitted by the leaves burns up the hydrogen.

The same thing occurred with the *Antirrhinum*, but the action was slower. In both cases the leaves were slightly bleached, more decidedly so in the latter case; and as the water charged with carbonic acid rose in the vessel and covered them, they became greener again.

In all these experiments the plants were exposed to the constant light of a northern sky. The rapidity of cell formation in hydrogen gas observed in the case of *Convolvulus arvensis* is highly remarkable.

Putney, June 23, 1893.

THE ACTION OF SILICON ON THE METALS GOLD, SILVER, PLATINUM, AND MERCURY.

By H. N. WARREN, Research Analyst.

WITH regard to the action of silicon on the more common metals,—iron and copper,—so well known are the properties in general of these elements when combined, that little, if any, comment is required; but on passing to the more refractory metals a much wider field for study is presented. As recorded by the various handbooks of chemistry, silicon, when in the nascent state, converts platinum into a brittle silicide.

This is by no means, however, the only method available for preparing this compound; for on heating graphitoid silicon in contact with platinum to a full red heat, combination at once takes place, resulting in a brittle regulus, being fusible at a red heat, and breaking with a crystalline fracture, at the same time being difficultly soluble in acids. The same compound may be more readily formed by heating in a closed crucible a mixture of amorphous silicon and platinum-black under a layer of potassium silico-fluoride; the analysis of several samples thus obtained proved the existence of 10 per cent silicon. On the other hand, neither silver or gold present any great affinity towards silicon, but on heating a mixture of potassium silico-fluoride, metallic sodium, and either gold or silver in the amorphous condition to a high temperature, a well-fused regulus of silicide of the metal may be obtained. In the latter instance the alloy, containing as little as 5 per cent silicon, is almost as brittle as antimony, and resembles gold alloyed with a large proportion of silver. At the same time, although silicon possesses no considerable affinity towards either gold or silver, except when in a nascent state, still that affinity appears to be considerably enhanced by combining with either metal when in the fused condition a small quantity of an already prepared silicide. Thus, if on to the surface of a quantity of either silver or gold in the fused condition is ejected a few grains of an already prepared silicide of either gold or silver, complete mixture of the same at once ensues. This alloy, although containing but a minute percentage of silicon, may be raised to a much higher rate by the introduction of elementary silicon, which before this period showed even at elevated temperatures no special affinity, except when in a nascent form. Silver, when thus impregnated with from 10 per cent of silicon, becomes of a slightly red tint, resembling in appearance metallic manganese.

* Phipson, "Chemical Constitution of the Atmosphere from remote Geological Periods to the Present Time," CHEMICAL NEWS, vol. lxvii., p. 135.

The regulus, after being pulverised, is completely decomposed by the aid of concentrated hydriodic acid. As regards the action of silicon on metallic mercury, nothing very definite can at present be stated; but on subjecting a small vessel containing mercury in contact with an alcoholic solution of silicon fluoride to the action of a powerful battery, and afterwards subjecting the mercury to distillation, a small quantity of amorphous silicon was obtained, but whether silicon, when in a nascent state, combines with, or is soluble in, mercury still presents considerable doubt.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

A REVIEW OF RECENT INVESTIGATIONS UPON CARBOHYDRATES.*

By W. E. STONE.

THESE notes are intended to include the more important contributions to the subject during the past year without reference to technical matters.

In most cases the original papers are referred to for details, and only their leading features are given here on account of lack of space.

New Sugars.

Some new members of the group of natural sugars have been identified, of which the *Stachyose* (E. Schulze and A. von Planta, *Land. Versuch Stat.*, xl., 277; and xli., 123) is best characterised. It has been isolated from the tubers of *Stachys tubrifera*, where it occurs to the extent of 14 to 19 per cent of the fresh material. It is very sweet, without action on Fehling's solution, and with a specific rotation $(\alpha)_D = +147.9^\circ$. It belongs to the trisaccharides or "trioses," with a formula corresponding to $C_{18}H_{32}O_{16}, 3H_2O$. On inversion, it breaks up into dextrose, levulose, and galactose, but in different proportions than raffinose. Probably the molecule is larger than indicated by the above formula, and its inversion products are, galactose three parts, dextrose two parts, and levulose one part.

Fucose (Günther and Tollens, *Annalen d. Chemie*, cclxxi., 86) is another new sugar obtained by heating a species of alga (*Fucus*) with dilute sulphuric acid. It is strongly lævorotatory $(\alpha)_D = -75.96^\circ$, and shows marked multirotation; reduces Fehling's solution; yields an "osazon" melting at $158-160^\circ$, and has the formula $C_6H_{12}O_5$. It is isomeric with rhamnose. It yields methyl-furfural, and is regarded as a methyl-pentose. Calorimetric observations indicate that it is methyl-arabinose (Stohman and Langbein, *J. Prakt. Chem.*, [2], xlv., 305).

Agavose (Michaud and Tristan, *Am. Chem. Journ.*, xiv., 548) is an optically inactive sugar obtained from the juices of *Agave Americana*. After inversion it becomes lævorotatory $(\alpha)_D = -14.39^\circ$. It is very sweet, and reduces Fehling's solution about five-eighths as strongly as dextrose. It yields no mucic acid on oxidation. Further investigation of the sugar will be awaited with interest, as it is probably the source, by fermentation, of the alcoholic constituents of the Mexican "pulque."

Lupeose (E. Schulze, *Ber. d. Chem. Ges.*, xxv., 2213) is the name given to one of the insoluble amorphous constituents of the coat of the lupine seed. It is not a sugar, but yields on inversion galactose, levulose, and probably dextrose. It has previously appeared in literature as β -galactan (E. Steiger).

Progress on Synthetical Lines.

The series of syntheses accomplished by Fischer and reviewed in *Agricultural Science* (vol. vi., 166) has been

* From *Agricultural Science*.

less actively extended of late. Admitting any ketone or aldehyd alcohol to be a sugar, as Fischer proposes, then the glycol aldehyd, CH_2OH, CHO , which he has prepared sparingly, is the simplest form of a sugar. There is an objection to this on the ground of optical inactivity, although it otherwise satisfies the conditions, reducing Fehling's solution, combining with phenylhydrazin and polymerising to tetrose, $C_4H_8O_4$ (E. Fischer and Landsteiner, *Ber. d. Chem. Ges.*, xxv., 2549).

It has also been shown that mucic acid could be reduced to an inactive monobasic acid which was then separable into two optically opposed isomers; one of which was d. galactonic acid; the other, a new body, l. galactonic acid. The inactive acid was reduced to inactive galactose, which after undergoing partial fermentation left behind l. galactose, thus completing the series of optical isomers of galactose (E. Fischer and J. Hertz, *Ber. d. Chem. Ges.*, xxv., 1247). By reduction of phenyl-tri-oxybutyric acid by methods practised in his previous investigations, Fischer has also succeeded in producing a phenyl-tetrose, combining the properties of a benzine derivative and a sugar (E. Fischer and Stewart, *Ber. d. Chem. Ges.*, xxv., 2555).

Pentoses.

Of the sugars which have already obtained a place in literature, the pentoses have received a good share of attention of late. Considerable effort has been expended in the development of methods for determining the amount of pentosans in vegetable materials. As a result of studies by Tollens and his pupils, the method of distilling with HCl, and precipitation and weighing of the furfural by phenylhydrazin is regarded as satisfactory. By this method they obtained from xylose direct 52 per cent and from arabinose 43 per cent of furfural, and have shown that many crude materials contain large amounts of pentosans; for instance, wheat straw yielded 21.90 per cent; corn cobs, 30.94 per cent; and brewers' grains, 27.00 per cent of furfural (Tollens, Günther, and de Chalmot, *Land. Versuch Stat.*, xl., 11-17; Tollens and Flint, *Ber. d. Chem. Ges.*, xxv., 2912).

Bearing on this furfural reaction as a means of determining the pentoses and pentosans, it has been found that glucuronic acid and its derivatives also yield furfural in appreciable quantities, although under no ordinary circumstances would this lead to confusion on account of the rarity of glucuronic acid (Tollens, Günther, and de Chalmot, *Ber. d. Chem. Ges.*, xxv., 2569).

Experiments undertaken to ascertain if the pentoses (xylose) might be substituted for other sugars in the food of diabetic patients, have shown that the former, even though very soluble, are little if at all assimilated, and may be detected in the urine in a short time after consumption. Slight traces of the pentoses may be recognised in the urine by means of the phloroglucin reaction (*Central Bl. f. Med. Wissens.*, W. Ebstein, 1892, 577; E. Salkowski, 1892, 593. *Archiv. f. Path. Anat.*, W. Ebstein, cxxix., 401).

Investigations directed at the digestibility of the pentosans contained in feeding stuffs, shows that they are by no means completely digestible, probably much less so than the other amorphous carbohydrates of the same solubility (W. E. Stone, *Am. Chem. Journ.*, xiv., 9; *Agricultural Science*, vii., 6).

Neither of the pentoses has yet been found in nature as a free occurring sugar, although late researches seem to indicate the presence of slight traces in the green organs of plants as migratory material between assimilating organs and reserve tissues (G. de Chalmot, *Am. Chem. Journ.*, xv., 21).

On the other hand, the occurrence of the pentosans in new materials has been frequently noted. Xylose has been prepared from *Luffa* (fibro-vascular tissue of the fruit of a species of *Cucurbitaceæ*) by direct hydrolysis (Tollens and Schulze, *Land. Versuch Stat.*, xl., 381; also Tollens and Allen, *Ann. d. Chem.*, 260, 297). The pentosans of brewers' grains, already shown to yield both xylose

and arabinose, have been found to consist principally of the mother substance of xylose (Tollens and Schulze, *Land. Versuch Stat.*, xl., 367). The mucilage produced from quince seeds also yields xylose on inversion (*Ibid.*, 382; also Tollens and Gans, *Ann. d. Chem.*, ccxlix., 245). Xylose has been found in the liquors resulting in the manufacture of wood pulp by the "sulphite" method (Tollens and Lindsey, *Ann. d. Chem.*, cclxvii., 341). It has also been prepared from the alkaline liquors resulting from the pulping of straw in paper making (Stone and Test, *Am. Chem. Journ.*, xv., 195). In the coffee berry a pentosan has also been found, but the derivative pentose was not isolated (E. E. Elwell, *Am. Chem. Journ.*, xiv., 473). In this case the pentosan seemed to be present as a complex of pentosan and galactan, for the apparently homogeneous substance yielded both furfural and mucic acid. A similar complex has already been proven in the gum exuding from the peach tree (Stone, *Am. Chem. Journ.*, xii., No. 6). Such a galacto-araban has also been found in the seeds of certain Leguminosæ, and in the bran of wheat and rye. These pentosans seem to be intimately connected with the ultimate cellular frame-work of the plant, and persist in connection with the fibre after the action of strong acids and alkalis (E. Schulze, *Chem. Centralblatt*, 1892, i., 701).

The specific rotation of xylose has been carefully worked out and found to be somewhat dependent upon temperature and concentration; for 10 per cent solution and 20°, $(\alpha)_D = 18.794$ (Tollens and Schulze, *Land. Versuch Stat.*, xl., 384).

The resistance of arabinose and xylose to the continued action of dilute sulphuric acid has been found to be considerable. After twenty hours boiling with 4 per cent acid only slight decomposition had occurred, and after thirty-two hours 84 per cent of arabinose and 73 per cent of xylose were unchanged (Tollens and Schulze, *Land. Versuch Stat.*, xl., 379).

Arabinose, which is not susceptible to alcoholic fermentation by yeast, succumbs to an organism named *Bacillus ethaceticus*, yielding ethyl alcohol and acetic acid, CO₂ and H, with traces of succinic acid. It appeared that more acetic acid in proportion to the alcohol was found than by a similar fermentation of dextrose or glycerin (Frankland and McGregor, *Journ. Chem. Soc.*, lxi., 737).

Hexoses.

Dextrose.—Some new sources or occurrences of dextrose have been announced. From the mucilage obtained from the coatings of quince seeds it was obtained by hydrolysis (R. W. Bauer, *Land. Versuch Stat.*, xxxix., 469); from the cellulose left in the manufacture of wood pulp by the "sulphite" process, in the same way (Tollens and Lindsey, *Annalen d. Chem.*, cclxvii., 370); by decomposing digitonin by heating with hydrochloric acid (H. Kiliani, *Archiv. der Pharm.*, ccxxx., 261).

Of unusual interest is the additional proof of dextrose in the blood, which has long been known to reduce Fehling's solution, ferment, and rotate polarised light. From blood has now been prepared a phenylhydrazin compound corresponding wholly with phenyl-glucosazon (Max. Pickardt, *Zeit. f. Physiol. Chem.*, xvii., 217). An octacetyl derivative of dextrose, as announced by Franchimont and later by Ewig and Koenig, has been found to be after all only a pentacetyl compound existing in isomeric form, one of which is optically inactive, and the other dextro-rotatory (A. Franchimont, *Recueil d. Travaux Chim. de Pays bas*). It has been noted that acetone is appreciably soluble in solutions of dextrose, as well as other sugar, and this solubility at different concentrations and temperatures has been determined (W. Krug, *Am. Journ. Anal. and Appl. Chem.*, 1892, 189).

Levulose has been identified in thirty-six different species of fungi (E. Bourquelot, *Wochenschrift f. Brauerei*, viii., 908). Its specific rotation, as determined

by calculation from the constants of invert sugar and of dextrose, is announced as $(\alpha)_D = -106^\circ$, or $(\alpha)_D = -93.8$ (O'Sullivan, *CHEM. NEWS*, lxx., 165); and these numbers agree with those of Ost (-93.01) and Tollens (-92.5) fairly well. A former statement that levulose yielded mucic acid upon oxidation has been reviewed by its author and found to be incorrect (Von Lippmann, *Berichte der Chem. Gesell.*, xxv., 3216). A method for the quantitative determination of levulose in the presence of dextrose and sucrose will be mentioned later.

Galactose has been obtained from the liquor resulting from the sulphite wood-pulp process (Tollens and Lindsey, *Annalen d. Chem.*, cclxvii., 341), and from the complex *lupeose* in common with levulose and dextrose (E. Schulze, *Berichte d. Chem. Gesell.*, 2213); also by the decomposition of digitonin by means of alcoholic hydrochloric acid (H. Kiliani, *Archiv. f. Pharm.*, ccxxx., 261). The synthetic inactive galactose has already been noted.

Mannit and Mannose.—Mannit has been found in many different species of fungi amounting in some to from 2 to 15 per cent (E. Bourquelot, *Wochenschrift f. Brauerei*, viii., 908). Mannose was found with other sugars in the sulphite liquors from wood pulp (*loc. cit.*), and has been obtained by inversion of one of the more easily soluble forms of cellulose ("hemi-cellulose"). In the more resistant "cellulose" a substance is thought to exist (mannoso-cellulose) which on inversion yields dextrose and mannose (E. Schulze, *Chem. Centralblatt*, 1892, i., 701). From experiments, the physiological action of mannose is said to resemble that of galactose; it is excreted strongly in the urine, and is accompanied by the occurrence of small amounts of glycogen (Cremer, *Centralblatt f. Physiologie*, vi., 396).

Bearing upon the constitution of mannit is the fact that it forms a hexaiodide which may be transformed into a secondary inactive alcohol. This on being acted upon by fungi left behind a dextro-rotatory product which was regarded as ethyl-propyl-carbinol (Combes and LeBel, *Bull. de la Soc. Chim. de Paris*, [3], vii., 551).

Dulcitol and Mannit are subject to a kind of fermentation by *Bacillus ethaceticus* (see arabinose) yielding ethyl alcohol, acetic acid, succinic acid, CO₂, and H (Frankland and Frew, *Journ. Chem. Soc.*, lxi., 264). Conflicting statements as to the activity or inactivity of dulcitol have been current; the acetyl compounds have been said to be active. Upon a re-investigation they prove to be inactive, and thereby almost the last obstacle to the theory of optical activity in the sugar group is removed (A. W. Crosby, *Berichte d. Chem. Gesell.*, xxv., 2564).

Isodulcitol or Rhamnose, C₆H₁₂O₅, although no new substance, has been of uncertain classification. It has been found to yield methylfurfural when heated with HCl, and not levulinic acid, which shows that its nucleus is a pentose and not a hexose. Its specific rotation for anhydrous material is $(\alpha)_D = 9.43^\circ$ at 20° C. (Schnelle and Tollens, *Annalen d. Chem.*, cclxxi., 62). By determination of its temperature of combustion when compared with those of xylose and arabinose is indicated a relation to the former (Stohman and Langbein, *Journ. Prakt. Chem.*, [2], xlv., 305). (See Fucose). It is, therefore, fairly well established as a methyl-xylose.

Disaccharides.

The presence of *sucrose* has been determined in the coffee berry, where from 6.24 to 6.34 per cent was found in the alcoholic extract (E. E. Elwell, *Am. Chem. Journ.*, xiv., 473). The solubility of acetone in solution of cane-sugar of strengths from 10 to 50 per cent, and at temperatures from 15° to 35°, has been determined (W. H. Krug, *Jour. Anal. and App. Chem.*, 1892, 89). Maltose has also been studied in the same respect.

It was noted some years ago that *lactose* existed in two optical modifications. In the light of recent developments the author has thought best to review his work, and finds it to have been correct; moreover, these modifications have the same molecular weight, refractive

exponents, and degrees of dispersion. The statements of Herzfeld about the formation of an octacetyl derivative are substantiated by the same author (M. Schmöger, *Berichte d. Chem. Gesell.*, xxv., 1452).

Isomaltose may now be prepared with comparatively little trouble by acting on starch-paste with diastase at 67–69°, and separation from by-products by treatment with strong alcohol. In this way 20 per cent of the starch may be obtained as isomaltose (Lintner and Düll, *Zeit. f. das ges. Brauereiwesen*, xv., 145).

Trisaccharides.

Raffinose is said never to occur in the sugar-beet itself, and hence does not interfere with the determination of sucrose in that material. It is a product of manufacturing processes, but is no molasses former, and does not prevent crystallisation of the sucrose. The only reliable method for determining raffinose in sugar products is that of Clerget as modified by Herzfeld (A. Aulard, *Zeit. für Rüb. Zuck. Ind.*, 1892, 752).

Miscellaneous.

The action of diastase upon starch has been studied by different investigators, and the products seem to be very complex; beside the isomaltose already mentioned there seems always to be found malto-dextrin, achroo-dextrin, erythro-dextrin, and dextrin (Anton Schiffer, *Neue Zeit. f. Rüb. Zuck. Ind.*, xxviii., 167). Some new methods for the analytical determination of starch have also been presented, for which see below.

Perseit has held a rather indefinite place with regard to the better studied carbohydrates. Fischer found that the heptatomic alcohol derived from the reduction of manno-heptose was identical with the natural perseit, thus establishing its synthesis. By reduction with hydroiodic acid it becomes C_7H_{14} , called heptin, which has been found to be identical with toluol-hexahydrin, thus presenting an unexpected transition from the fatty to the benzene hydrocarbons (L. Maquenne, *Compt. Rend.*, cxiv., 1066). Perseit is optically active (ævo-rotatory). Upon addition of a soluble molybdate to its watery solution it becomes dextro-rotatory (D. Gernez, *Compt. Rend.*, cxiv., 480).

Multi-rotation.

The well-known property of many sugars to exhibit a different degree of rotation immediately after solution in cold water, than after standing some hours, has been carefully studied for several sugars not previously investigated and several of their derivatives. An interesting observation in this connection was, that if a very small amount of ammonia be added to such a solution the multi-rotation disappears. 0.1 grm. of ammonia suffices to produce this result, and a larger amount even decreases the normal rotation (Tollens and Schulze, *Land. Versuch Stat.*, xl., 387).

Analytical.

With regard to the saccharimetric coefficient for glucose the suggestion is made of a new constant, by which each degree of the saccharimeter should represent not 3.28 grms. of anhydrous dextrose in the litre as at present, since this is based on the specific rotation of dextrose calculated to anhydrous material. In place of this, 2.06 grms. of water-free dextrose in the litre is said to give a rotation of one degree, and should be the true saccharimetric constant (L. Grimbert, *Four. Prakt. Chem.* [5], 26, 253).

For the determination of invert sugar by Herzfeld's method, a new constant for small quantities of sugar has been worked out. It was not always possible to use 10 grms. of material as demanded by Herzfeld's method, nor was it correct to use 5 grms. of material and multiply

the results by two. A new table for 5 grms. has been completed (see original paper, or *Chem. Centralbl.*, 1892, 2, 997). By the method of least squares this formula has been deduced, x indicating copper obtained. Invert sugar = $0.3164 + 0.010054x + 0.000,003,021x^2$ (J. Baumann, *Zeit. Verein f. Rüb. Ind.*, 1892, 824).

The method for determining dextrin in the presence of dextrose and maltose, by the action of mercuric cyanide as proposed by Wiley, has been reviewed by treating each of the substances separately with mercuric cyanide in alkaline solution. It was found that when the action was continued two minutes, the rotatory power of the dextrose was destroyed and that of the maltose much reduced, but that of the dextrin was also perceptibly diminished; which would indicate that the method was not wholly reliable (J. A. Wilson, *CHEM. NEWS*, lxx., 169).

For the determination of sucrose, dextrose, and levulose in mixture, an ingenious combination of gravimetric and optical operations has been proposed, which, according to the author's results, is reliable. A solution is carefully prepared, and its density and rotatory power determined; in a weighed portion the amount of reducing sugar is determined with Fehling's solution gravimetrically: another weighed portion is inverted, and the total reducing sugar in it determined. From the data thus obtained, viz., rotation and reducing sugar before and after inversion, can be calculated, by algebraic formulæ, the amounts of each of the sugars present. The original paper must be consulted for details (F. G. Wiechmann, *School of Mines Quarterly*, xiii., No. 3; *CHEM. NEWS*, lxxvi., 237).

Formulæ for the determination of sucrose and raffinose in mixtures are proposed as follows:— $S = K_1A + K_2B$ and $R = K_3A - K_4B$, in which A and B are the direct and indirect polarisations of normal weights, and K_1 , K_2 , K_3 , and K_4 are temperature coefficients (Mehay, "Sucrerie Ind. et Coloniale," *Chem. Centralbl.*, 1892, i. 508).

For the determination of starch a new method depends upon (1) the solubility of starch when heated with salicylic or benzoic acid; (2) the rotation of polarised light by such a starch solution; and (3) the fact that rotation is proportional to the quantity of starch. A weighed quantity of starch (2.688 grms. for Laurent's polariscope) is boiled with 80–90 c.c. water and 0.4–0.5 grm. of salicylic acid forty to fifty minutes, filled to a volume of 200 c.c. with addition of ammonia, filtered, and polarised in 400 m.m. tube. The reading of circular degrees corresponds to percentages. The method may be applied to commercial starch or potatoes, or similar materials (A. Baudry, *Chem. Centralbl.*, 1892, i., 339 and 509).

Another method for determining starch is to invert with dilute nitric acid and polarise the solution; in the case of cellular tissues the starch must first be extracted by boiling with oxalic acid, and then inverted with nitric acid (Guichard, *Bull. Soc. Chim. de Paris*, [3], vii., 554).

Heat Values, &c.

The researches of Stohmann and Langbein upon the heat values of the carbohydrates, which have been extended over considerable time, is now well completed. Their work is of high character, but too extended for details in this space. As a general result they find that isomers give approximately the same values, and for homologous series the different members have a fairly constant difference. The heat value of the pentoses is about 560 calories; the methyl-pentoses, 711–718 cal.; hexoses, 672 cal.; disaccharides, 1351.5 cal.; and the polysaccharides (starch, &c.), 677.75 cal. (*Fourn. Prakt. Chem.* [2], xlv., 305).

In the same way the study of the higher alcohols shows that for each addition of CH_2O in the homologous series, there is a constant increase of 113 cal., which holds true of the synthetic gluco-heptit when compared with mannit (J. Fogh, *Compt. Rend.*, cxiv., 920).

THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Concluded from p. 296).

Chromium.

A SATISFACTORY method for the determination of chromium has yet to be devised. In the methods generally employed the iron or steel is dissolved in the usual acids, the silica separated by filtration, and the chromium, together with the iron, precipitated in the filtrate by ammonia. After washing and drying, the precipitate is mixed, contained in a platinum crucible, with five times its weight of equal portions of sodium carbonate and potassium nitrate, and fused; the cold fused mass treated with water, the insoluble oxide of iron separated, and the filtrate acidulated with hydrochloric acid, mixed with a slight excess of alcohol, and boiled, whereby the alkaline chromate is reduced. After expelling the excess of alcohol a slight excess of ammonia is added, the solution boiled, the resulting chromium hydrate filtered off, washed, ignited, and weighed as oxide of chromium, (Cr_2O_3), which contains 68.62 per cent of chromium. Another method is to convert the chromium, contained in a solution as peroxide, into chromic acid, by passing a current of chlorine gas through, after nearly neutralising with sodium carbonate and adding an excess of sodium acetate. Upon boiling, the excess of chlorine is driven off and the iron precipitated, the latter being separated by filtration. The chromic acid in the filtrate is then reduced with alcohol and hydrochloric acid, the chromium precipitated as hydrate with ammonia, and weighed as oxide. Instead of precipitation as hydrate with ammonia, it may be thrown down as lead chromate by the addition of lead acetate.

The methods in which the solution remaining after the separation of the silica is employed for the determination of the chromium, do not furnish accurate results, as in the majority of instances a portion of the silica obtained invariably contains an insoluble phosphate, which carries a portion of the chromium along with it. This is especially the case with specimens containing notable quantities of phosphorus.

Another method, which in our experience has given very good results, is as follows:—One or two grms. of the metal, according to the amount of the chromium presumably present, contained in a beaker, is dissolved in 40 to 50 c.c. of hydrochloric acid, and the solution gently evaporated to dryness, the employment of an excessive heat being carefully guarded against. The cakey mass of chlorides is now broken up as completely as possible and removed to a porcelain dish, while the portions still adhering to the containing vessel are dissolved in a few drops of hydrochloric acid, the resulting solution rinsed into a platinum crucible with the least possible quantity of wash water, and the whole evaporated to dryness. To the contents of the platinum crucible, when dry, add the mass of chlorides contained in the porcelain dish, and intimately mix the whole with five times its weight of a fusion mixture composed of equal weights of sodium carbonate and potassium nitrate.† Place a cover on the crucible and fuse, employing at first a gentle heat, but gradually increasing to bright redness, for half an hour, whereby the oxide of chromium is converted into alkaline chromate. When cold the crucible is placed in a porcelain dish, covered with water, and heated until the fused mass is completely detached, when, after washing, it is withdrawn. The resulting solution is mixed with a few drops of alcohol, heated to boiling for an hour or so to reduce any alkaline manganate present, and allowed to stand until the oxide of iron has settled. Separate the oxide of iron by filtration through a double Swedish

filter,* and wash the filter well with hot water. The filtrate is now acidulated with hydrochloric acid, excess of alcohol added, and the solution boiled; this results in the reduction of the alkaline chromate. The boiling is continued until the whole of the alcohol is expelled, and, when this is effected, to the solution add the slightest possible excess of ammonia, and digest at a gentle heat until the supernatant liquid is colourless. Collect the resulting precipitate; chromium hydrate, and filter; wash well, dry, ignite, and weigh as oxide of chromium (Cr_2O_3), containing 68.62 per cent of chromium.

In the *CHEMICAL NEWS* some time ago Messrs. Arnold and Hardy described a method in which the chromium is precipitated as a phosphate by means of sodium phosphate. The authors dispense with the filtering off of the iron oxide by taking a portion of the clear extract of the fusion equivalent to a known weight of the metal. They also condemn the employment of alcohol for reducing the chromate, and further state that it is not essential.

In steel, chromium may be very easily estimated by Galbraith's volumetric method. Two or three grms. are dissolved in dilute sulphuric acid (1 to 6 H_2O), after complete solution add crystals of potassium permanganate in somewhat slight excess, boil quickly until the pink colour disappears, and, if considered necessary, a few more crystals, and again boil; filter from precipitated manganese oxide. The filtrate contains the chromium as chromic acid. Add a weighed quantity of ferrous sulphate, "or, better, dissolve pure iron in dilute sulphuric acid and add to filtrate." Then determine the excess of iron unoxidised with standard bichromate solution. This quantity, deducted from the total amount used, equals iron oxidised by the chromic acid, which, multiplied by 0.3101 = chromium in the metal.

Example.—Two grms. of steel dissolved in HCl, 0.50 gm. pure iron added to solution iron unoxidised 0.175 gm.—

$$\frac{0.50 - 0.175 \times 0.3101}{2} = 1.52970 \text{ chromium.}$$

This method is accurate, and, in our own experience, very reliable.

Small quantities of chromium may be estimated by comparing the green colour of a solution containing the metal in the form of CrO_3 with a standard solution containing a known quantity of chromium. It is well known that chromium considerably modifies the value of steel, and at the present moment it seems desirable to occasionally test steels for this element.

Phosphorus.

As regards the determination of this constituent many so-called "rapid" methods have been published, but we are not aware of one that really has any advantage, either for rapidity or simplicity, over the one we described in our first article. Usually the percentage of phosphorus in iron varies directly with the character and kind of ore used. Variations in blast-furnace working, leading to irregular reduction of silica and sulphur, appear to have little or no effect on the phosphorus contained in the ore, the whole of which practically passes into the iron, unless a very crude or white iron is made; in the latter case some proportion of the phosphorus passes into the slag.

Calcium, Magnesium, Aluminium, Nickel, and Cobalt.

Aluminium, calcium, and magnesium are sometimes given in the analysis of iron and steel, but they are seldom looked for, with the exception of aluminium, which has recently been added to fused malleable iron and steel in small quantities, and is said to improve its quality, as also to facilitate the casting of the metal by

* From *Industries*.

† If the solution and evaporation be effected in the platinum crucible, this will be unnecessary.

* Necessary on account of the fine state of division in which the oxide of iron exists.

lowering the fusing points, thus rendering it more fluid, producing sound malleable iron castings very free from honeycomb and blow-holes. This, however, has been questioned.

Calcium and magnesium may be determined by first freeing the original acid solution of the metal from iron, aluminium, and manganese, as previously described, evaporating the resulting filtrate to a very small bulk, exercising extreme care to avoid dust, &c. (apt to contain both calcium and magnesium), rendering alkaline with ammonia, precipitating the calcium by means of ammonium oxalate, and boiling. The solution is filtered through a Swedish filter, thoroughly washed, transferred to a crucible, and the precipitate converted by ignition at a white heat into calcium oxide, CaO , in which state it is weighed. CaO contains 71.43 per cent of calcium (Ca).

To the filtrate remaining from the precipitation of the calcium, contained in a porcelain dish, add some nitric acid, evaporate to dryness, and heat strongly. Repeat this operation two or three times, finally dissolve the dry residue in water, filter if necessary, add to the solution a little ammonium chloride, make ammoniacal,* add excess of ammonium phosphate, agitate the containing vessel well, and allow to stand in the cold for twenty-four hours. Collect the resulting precipitate of ammonium-magnesium-phosphate on a Swedish filter, wash with water containing ammonia, detach as completely as possible from filter-paper, ignite, add filter-ash, and weigh as magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, containing 21.62 per cent of magnesium.

Determination of Aluminium.

The iron and alumina are precipitated together by ammonia and ammonium acetate, from an acid solution of the metal, as in the determination of manganese, the precipitate transferred to a silver dish, and boiled for some time with a strong solution of pure caustic potash, the insoluble portion filtered off, thoroughly washed with hot water, and to the filtrate hydrochloric acid is carefully added until the precipitate alumina formed is redissolved. Neutralise the solution, which must be only slightly, but at the same time distinctly, acid with ammonia, and precipitate the alumina with ammonium carbonate, heat to boiling, collect the resulting precipitate on a filter, copiously wash with water until free from alkali, ignite, and weigh as alumina (Al_2O_3), which contains 53.40 per cent of Al.

As great difficulty is experienced in washing out the alkali, it is advisable to dissolve the Al_2O_3 , after weighing, and re-precipitate. This method is not suitable for the determination of small quantities of alumina. A better method is to partly reduce the iron to the ferrous state (FeO); on treating as above Al_2O_3 is completely precipitated, together with a small excess of Fe_2O_3 , and the alumina is thus more easily separated on boiling with potash. Or, if the amount of Fe_2O_3 be very small, this latter can be estimated by the colorimetric method, and deducted from the total weight of Fe_2O_3 and Al_2O_3 previously weighed. Or, the well-known method of Stead's may be used in lieu of the methods given; but in our practice we find the second of the foregoing to be sufficiently accurate.

The quantity of nickel and cobalt contained in iron and steel are, as a rule, very small. For the determination of the metals, the filtrate remaining after the separation of the silicon, as previously described, is diluted to a large volume, cooled, made neutral with sodium carbonate, the iron precipitated by the addition of a large excess of sodium acetate, the solution boiled for some time, and the basic acetate of iron filtered off. According to Crookes, the whole of the nickel and cobalt will be

contained in the filtrate. It is, however, advisable to dissolve the iron precipitate in hydrochloric acid, and, after diluting largely and cooling, to neutralise with sodium carbonate, re-precipitate the iron with sodium acetate, boil, and filter, adding the filtrate to that remaining from the first precipitation. The volume of these mixed filtrates is considerably reduced by evaporation, after which it is made ammoniacal, ammonium sulphide added, the mouth of the containing vessel closed, and allowed to stand in a warm place for twenty-four hours.

The resulting precipitate of nickel, cobalt, and perhaps manganese, sulphides, are collected, digested in acetic acid to dissolve the manganese sulphide, and the residual sulphides washed, dried, and weighed. (For the method of separating the two metals, which is very complicated, see Dittmar's "Quan. Chem. Analysis," pp. 106 to 111.)

The methods herein described for the determination of chromium, titanium, arsenic, tungsten, &c., although the simplest and most rapid known to us, in a measure fail to meet the wants of the steel or ironworks' chemist, as, on account of the time consumed, regular daily determinations, as in the case of silicon, carbon, sulphur, &c., cannot be made. Naturally the steel-works' chemist rarely looks for these constituents, although it is very probable that these may often be present in iron and steel. Therefore the opportunities are few of comparing such analyses with the working of the metal, of fixing any limit as regards the maximum quantities of these allowable in steel or iron, or of determining to what degree the behaviour of the metal is affected when these are present in varying proportions.

Such methods would undoubtedly prove of incalculable value, but unfortunately they have yet to be devised, and until they are we are afraid the determination of the titanium, chromium, &c., as generally performed, will not prove of much real use.

THE CHEMICO-LEGAL EXAMINATION OF STAINS SUSPECTED AS CONTAINING BLOOD.

By H. STRUVE.

It was not my purpose to give an opinion on the chemico-legal examination of suspected blood spots, since I am at present engaged with the collation of my nearly twenty-five years' experience as expert for judicial chemistry to the Caucasian Civil Medical authorities—a task which will still engage me for some months. If I, nevertheless, enter upon this question my inducement lies in Prof. G. Janecek's pamphlet on the limits of scope of the spectrum of hæmatin and the hæmine crystals as evidence of the presence of blood.

On the observations and facts recorded by Janecek, I must simply declare that he has attributed to slight, unimportant, and, in part, incorrect, observations a weight in the chemico-legal decision on blood spots which they by no means deserve. This reply would be somewhat short and condemnatory, and therefore not demonstrative and convincing. On this account I think it justifiable to deal more in detail with the facts communicated by Janecek.

The chemico-legal diagnosis of suspicious spots as to the presence of blood is often submitted by the Courts to experts,* both as regards spots which are without doubt occasioned by blood, and of such minuteness as to be merely recognised with the lens. In such cases, the judges in most cases call for a definite reply to the three following questions:—

1. Are the suspected spots due to blood?

* A little tartaric or citric acid should be added to the solution previous to the addition of the ammonia and ammonium phosphate, to prevent the precipitation of any iron or alumina accidentally present.

* We believe that in Russia experts are not "called" respectively for the prosecution and the defence, but are consulted by the Courts.—Ed. C. N.

2. If to blood, is it human blood, or the blood of some other animal?

3. If blood is present, how old is the spot?

These three questions are the most usual, and to them the expert, according to the present state of our knowledge, can only reply that the spots submitted for examination are really blood spots or not; if blood, whether it has come from mammals, birds, or fishes. He cannot and must not go further, since we have not sufficiently well-founded facts for a certain diagnosis of the blood of different mammalia to admit of a definite reply, and conjectures and probabilities are here inadmissible.

The limits of the diagnosis of blood spots are clearly defined. The expert in his decision must remain purely objective, and leave all further inferences to the judges.*

The expert must uphold the results of his investigations with calmness and confidence; he has then fulfilled his task.

Among the blood stains which are laid before the expert for decision there belong those small spots which are often encountered on linen, clothing, and other objects. They are to be regarded as produced by the excretions of those parasitical animals which more or less frequently beset and annoy human beings, especially the lowest classes. These spots are very characteristically distinguished by their outward aspect, and can scarcely be mistaken for true blood spots. Among such stains we might include the dirt-spots of the common house fly, especially as, on suitable treatment, they display, according to Janecek, not merely the spectrum of hæmatin and of reduced hæmatin with a quite peculiar intensity, but readily give hæmine crystals.

Janecek assumes a peculiar blood-pigment in the excrements of flies, and hints at its possible connection with the myohæmatin found by McMunn in the muscles of invertebrates, and especially of insects. These facts completely clash with my experience. Years ago I undertook a series of experiments to which I was led by the phenomenon that if a fly is crushed a red spot is frequently obtained, occasioned by the colouring-matter of the eyes. I was particularly interested by this pigment, but on treating it with sodium chloride and acetic acid no crystals of hæmine were obtained. Other parts of the bodies of flies were often examined in the same manner, but there was no trace of crystals.

Not only flies, but spiders, were taken in hand, which had partly been fed for months under glass bells and had partly lived at large in the room. Their excreta were collected in sufficient quantity; it was not found possible to obtain from them crystals of hæmine, but the reactions of uric acid succeeded beautifully.

These experiments were concluded, laid aside, and forgotten, but were revived on reading Janecek's memoir. Still they were not decisive enough for the basis of my opinion. For this reason I used the opportunity, when spending this summer in Tiflis, in spite of the unusual heat and of the cholera epidemic, to make a further series of experiments relative to this question.

There was an excessive quantity of flies,† so that I could observe them as regards their diet and their excreta even more than was either necessary or pleasant. It appeared that the fly dirt was always modified by the substances which the flies had obtained for food. This was especially distinct with foods distinguished by a characteristic colour. If solutions of magenta, methylene-blue, or eosine were introduced into their food, these colours could be more or less distinctly recognised in the excreta even with a lens. Aniline ink was not rejected by the flies, as they are not select in their diet. If saccharine juices were offered them the excreta were adhesive, their colour was brownish, and the presence of sugar was detected in them

by means of Fehling's reaction. If flies were fed with solutions of blood, the excreta were darker, of a brownish red, and minute portions, if heated in the usual manner with sodium chloride and glacial acetic acid, showed the characteristic crystals of hæmine. All attempts to detect uric acid in these excreta gave negative results.

From these observations I conclude that blood pigment can be found in the excreta of flies only if they have had the opportunity of feeding on blood, but not otherwise.

I was still not content with these experiments, but wished to convince myself in general whether flies contain a pigment which may be even approximately compared in its properties to blood pigment.

In order to obtain the necessary material, a number of dead flies, more or less thoroughly desiccated, were treated in a glass flask with alcohol (70 per cent) at the temperature of a dwelling room. The alcohol gradually assumed a faint yellowish colour; it was filtered off and submitted to distillation. This extraction was repeated until it no longer became visibly coloured. On distillation, the extracts appeared more decidedly yellow, but on spectroscopic examination no absorption bands were recognised.

The residual flies were then shaken out with ammoniacal alcohol. There ensued very slowly a more decided colouration of the solution, which gradually became stronger. Nevertheless, such solutions, even when concentrated by distillation, showed no absorption bands. On further evaporation, such solutions became turbid from small particles of fat, which could be afterwards removed by shaking out with ether. The residual aqueous solution had a brownish colour, and an acid reaction. On complete evaporation they left a brown residue, soluble in water, which became carbonised at higher temperatures, leaving a rather sparingly combustible carbon. Chlorine, sulphuric acid, and alkalis could be detected in the ash, but lime, ferric oxide, and phosphoric acid were entirely absent. I have not been able to make a more complete examination of these extractive substances, partly from insufficiency of material, partly because it would have required too much time.

In conclusion, I add that if we call to mind that the blood pigments are partially soluble in alcohol at 70 per cent, but entirely in ammoniacal alcohol, and that such solutions on sufficient concentration are distinguished by characteristic absorption bands, we must infer that in the flies which I examined no pigments are present comparable in their properties with the well-known colouring-matters of the blood.—*Zeitschrift für Analytische Chemie*.

THE DETERMINATION OF BORON.

By HENRI MOISSAN.

At the outset of our researches on boron and its compounds, we were led to re-examine the different methods of determining boron. That which gave the best results and presented the most general applicability is the method of Gooch, founded upon the action of methylic alcohol upon boric acid. We have modified this process so as to render it more expeditious and to avoid the errors due to the evaporation of small quantities of boric acid.

Theory of the Determination.

The boron must previously be brought to the state of boric acid. This can be most generally effected by treating the substance under examination in a sealed tube. The mixture of boric and nitric acids is introduced into a flask. The boric acid is conducted away by pure methylic alcohol, and the liquid mixture is condensed in a Bohemian glass. The vapours are absorbed in ammonia, which is added to the liquid in the Bohemian glass after distillation. The liquid is poured upon a known weight of pure hydrated lime, weighed previously in the anhy-

* This prudent rule cannot be maintained under the English system of examination and cross-examination, which treats the expert as a partizan.—*Ed. C. N.*

† This observation refutes the assertion sometimes made, that flies leave any district on the outbreak of epidemics.—*Ed. C. N.*

drous condition, and contained in a platinum crucible. After remaining in contact for a quarter of an hour, it is evaporated on the water-bath at a temperature bordering upon 70°. It is then calcined, and weighed again as calcium borate. The increase of weight shows the boric anhydride. A simple calculation indicates the quantity of boron.

The evaporation on the water-bath is rather tedious, and requires to be carefully watched. The mass is then dried at a gradually increasing temperature, and the crucible is ignited before the blast, at first covered with its lid and then open. The refrigeration is effected over quicklime in a desiccator.

The lime employed in this process must be prepared in the crucible itself, and in a special manner. Pure calcium nitrate is ignited so as not to effect entire decomposition and to produce a basic nitrate easy to manipulate and to preserve. This compound is converted into quicklime by strong ignition when required. It is necessary to ascertain that the crucible contains nothing but quicklime, which is known by the constancy of its weight after several ignitions. A large excess of lime must be used. To 0.5 grm. boric acid the author's crucible contained from 8 to 10 grms. of lime.—*Comptes Rendus*.

RESEARCHES ON COBALT.

By HUGO REMMLER.

THE author studies the question whether metallic cobalt purified according to the ordinary methods, is a unitary body?

Induced by the observation that, contrary to the statements of the text-books, aqueous ammonia has a solvent action upon recently precipitated cobalt hydroxide, the author has endeavoured to bring carefully purified cobalt material into solution by the slow fractionated action of ammonia upon cobalt hydroxide, and to determine the atomic weights of the metals found present in the successive solutions.

The author was especially concerned to establish, by means of an extended and connected series of experiments, whether the material used for the determination of atomic weights—or at least a part of it—was absolutely homogeneous; that is to say, whether all the fractions of the material, or a larger number of successive fractions, had the same combining weight for the element in question.

From 1200 grms. cobaltous chloride, dissolved in water, cobalt hydroxide was precipitated by means of bromine water and potassa-lye. It was freed from every trace of potassium chloride by careful decantation and washing. The cobalt hydroxide was precipitated in two flasks, and the entire mass was treated with 10 litres of ammonia, being frequently shaken. In this manner 25 ammoniacal extracts were obtained.

The residues, on evaporating down these extracts, were all worked up in exactly the same manner. They were dissolved in hydrochloric acid precipitated with hydrogen sulphide, and after filtration they were precipitated with ammonium sulphide from an ammoniacal solution in presence of ammonium chloride.

The sulphides thus obtained were treated with 4 per cent, and afterwards with 7 per cent, hydrochloric acid, until the iron reaction disappeared, and were finally dissolved in aqua-regia. After neutralising with potassa-lye and acidifying with acetic acid, the cobalt was precipitated with potassium chloride and sodium nitrite. The cobalt salt was again subjected to the purification just described by solution in aqua-regia, treatment with hydrogen sulphide, precipitation with ammonium sulphide, and washing the sulphide with hydrochloric acid. Lastly, the cobalt sulphide was dissolved in aqua-regia, the solution evaporated down, the residue taken up

in water, the liquid freed from sulphur by filtration, and evaporated down with an excess of ammonia in order to convert any sulphuric acid into ammonium sulphate. The residue was ignited, and the cobalto-cobaltic oxide obtained was three times dissolved in hydrochloric acid, evaporated down with excess of ammonia, and ignited. Finally, the cobaltous chloride was converted into cobalto-cobaltic oxide by evaporation with nitric acid and ignition, and this was then submitted to examination.

The method which the author used for the determination of the atomic weight was essentially that pursued by Russell (*Journ. Chem. Soc.* [2], 1, 51), and afterwards by Zimmermann (*Lieb.ig's Annalen*, 232, 394).

In it the cobalt oxides, formed by the ignition of cobalt compounds in the air, are first converted into cobaltous oxide by ignition in indifferent gases, and the latter is then reduced to metal by means of hydrogen. From the loss of weight of the substance used on the reduction of the cobaltous oxide to metallic cobalt, there results the atomic weight of the metal referred to oxygen (O=16).

The first seven extracts were made with ammonia of different strengths and different durations of action; the extracts 8 to 25 were obtained by treatment with ammonia of sp. gr. 0.960; the digestion in 8, 9, and 10 being carried on, is each for eight days, and in the remaining extracts for ten days each. The determination of the fractions thus obtained yielded the following values for the atomic weight of cobalt:—

Fraction.	Atomic weight.
2	59.53
3	58.79
4	58.92
5	58.78
6	58.72
7	58.67
8	58.38
9	58.48
10	58.30
11	58.37
12	58.60
13	58.51
14	58.65
15	58.83
16	58.79
17	58.86
18	58.52
19	58.53
20	58.65
21	58.77
22	58.78
23	58.44
24	58.53
25	58.48

To check the accuracy of the determinations of the atomic weights of the twenty-four cobalt proportions, the atomic weights of three fractions selected at hazard were determined in duplicate, whereby results were obtained which differed from each other at most only in the second decimal places.

No determination of the atomic weight of fraction No. 1 was made, as the quantity of cobalto-cobaltic oxide obtained was too small.

From the above table it is apparent that the cobalt metals occurring in the different fractions between 58.9 and 58.3, and their difference according to the check experiments, cannot be due to analytical error.

The author gives various causes for the striking phenomenon that from the 2nd to the 10th fraction the values decrease, and then from fraction 10 to 18 or 19 increase with tolerable regularity, and then again become smaller.

Since the material, as it appears from the investigation, is not homogeneous, the hydroxide may be attacked by ammonia differently, according to differences of temperature such as occur in the course of a year. In a

mixture of two hydroxides, one constituent may have a different solubility in the solvent used than in a solution of the second constituent in the same solvent.

The author arrives consequently at the same conclusion as Gerhardt Krüss and F. W. Schmidt, that cobalt carefully purified by known methods is not a unitary substance. — *Zeit. Anorgan. Chemie*, ii., 442; *Zeit. Anal. Chemie*, xxxii., 273.

IRON AND ALUMINIUM IN BONE-BLACK: THEIR QUANTITATIVE DETERMINATION.

By Dr. F. G. WIECHMANN, Columbia College, New York.

THE determination of iron and aluminium in bone-black has thus far been commonly effected by the so-called ammonia-acetate method, which, until quite recently, has also been the favourite method employed for the determination of the constituents mentioned in mineral phosphates.

As this method, however, is open to serious objections, it was decided to test its accuracy, and to compare the results obtained with those yielded, respectively, by the method of E. Glaser (*Zeitsch. Angew. Chemie*, 1889, p. 636) and by the combination of Glaser's method with that of A. Stutzer (*Zeitsch. Angew. Chemie*, 1890, p. 43), first suggested by R. Jones (*Chemiker Zeitung*, 1890, p. 269) for the analysis of fertilisers.

For valuable analytical work performed in this connection, the writer's thanks are due to his assistant, Mr. E. C. Brainerd.

The schemes of analysis used in this investigation are minutely given in the following directions:—

Method I.—Acetate of Ammonia Process.

(This method is based on the solubility of calcium phosphate in acetic acid, and on the insolubility of the phosphates of iron and aluminium in this medium).

1. Powder sample. 2. Dry thoroughly. 3. Weigh out 3.0 grms. 4. Dissolve in distilled water + 25 c.c. HCl (conc.), boiling gently for one hour. 5. Filter. 6. Wash residue on filter until the wash-water no longer reacts for Cl with AgNO₃. 7. Add excess of BaCl₂, boil till BaSO₄ is granular. 8. Filter. 9. Wash the BaSO₄ on the filter till no more reaction for Cl with AgNO₃. 10. To filtrate and wash-waters combined add NH₄OH until the precipitate formed begins to appear permanent, and boil. 11. Then add acetic acid to pronounced acid reaction. 12. Filter. 13. Wash the precipitate well. 14. Dry, ignite, weigh. 15. Regard the precipitate as FePO₄ + AlPO₄, calculate to Fe₂O₃ + Al₂O₃, and so report.

Method II.—Glaser's Method.

(In this process the calcium is removed from an alcoholic solution by means of sulphuric acid before the precipitation of the iron and aluminium is effected).

1. Powder sample. 2. Dry thoroughly. 3. Weigh out 5.0 grms. 4. Dissolve in distilled H₂O + 30 c.c. HCl (conc.) + 10 c.c. HNO₃ (conc.). 5. Make the solution up to 500 c.c. with distilled water. 6. Filter. 7. Of the filtrate take 100 c.c. (equal to 1.00 gm.), place in a 250 c.c. flask, add 25 c.c. H₂SO₄ (conc.). Shake frequently, and allow to stand for five minutes. 8. Add absolute ethyl alcohol, cool, fill up to the mark with alcohol, and shake well. 9. As volume contraction will take place, fill up to the mark repeatedly with alcohol, and shake each time. Continue this filling up to the mark until no more contraction takes place. 10. Allow the solution to stand for twelve hours. 11. Filter. 12. Of the filtrate take 100 c.c. (= 0.4 gm.), place in a large platinum dish on a water-bath, and heat until all the alcohol is removed. 13. Wash the remaining solution into a beaker with 50 c.c. of distilled water. 14. Heat to boiling, and then re-

move the flame. 15. Add NH₄OH very carefully to alkaline reaction. 16. Boil until the ammonia is completely expelled. 17. Filter. 18. Wash the precipitate thoroughly with boiling distilled water. 19. Dry, incinerate, weigh. 20. Regard the precipitate as FePO₄ + AlPO₄, calculate to Fe₂O₃ + Al₂O₃, and so report.

Method III.—Combination of the Methods of Glaser and Stutzer.

(Stutzer's method consists essentially in precipitating the iron and aluminium, principally as phosphates, in a solution of ammonium acetate; treating this precipitate with a solution of ammonium molybdate to remove the phosphoric acid as phospho-ammonium molybdate; filtering out this precipitate, and in the resulting filtrate precipitating the iron and aluminium as hydrates, by ammonium hydrate; drying and igniting this precipitate, weighing it as Fe₂O₃ + Al₂O₃, and reporting it as such).

The following scheme, it is believed, offers all the advantages of both the Glaser and the Stutzer methods.

Proceed exactly as in Method II., up to and inclusive of section No. 18. Then continue as follows:—

1. Place filter and contents in a beaker which contains 150 c.c. molybdic solution* at a temperature of about 40° C. 2. Keep the mixture at a temperature of about 65° C. for from twelve to fifteen hours. 3. Filter out the precipitate. 4. Wash the precipitate thoroughly with NH₄NO₃ solution (1:10). 5. To filtrate add NH₄OH till it is well alkaline. 6. Heat for two or three hours over a gentle flame, replacing any loss by evaporation by the addition of water and ammoniac hydrate. 7. Filter out the precipitate. 8. Dissolve this precipitate from the filter with HCl. 9. Precipitate with NH₄OH, and boil out all free ammonia. 10. Filter. 11. Wash precipitate, dry, incinerate, and weigh. 12. Regard the precipitate as Fe₂O₃ + Al₂O₃, and so report.

The mixture on which these three methods were tested consisted of—

Tri-calcic phosphate	20.00	grms.
Aluminium sulphate	0.10	„
Ferrous sulphate	0.10	„

These amounts of the sulphates of iron and aluminium corresponded to 0.67 per cent of Fe₂O₃ + Al₂O₃, as was ascertained by analysis.

The mixture was dissolved in H₂O + HCl, and made up to 500 c.c. 24.75 c.c. of this solution contain 1.00 gm. of the dry substance.

In method I., used 3.00 grms.; in Method II., 1.00 gm.; in Method III., used 1.00 gm. of the "dry substance" for analysis.

Results of Analysis.

		Method.		
		I.	II.	III.
		Per cent.	Per cent.	Per cent.
Fe ₂ O ₃	Present	..	0.67	0.67
+ Al ₂ O ₃	Found	..	0.56	0.63

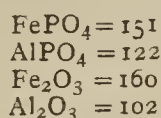
Method I. has evidently yielded the least satisfactory result.

Examining into its merits, it is readily seen that this method, as previously stated, is open to several serious objections: phosphate of aluminium is quite soluble in an excess of acetic acid; the precipitate of the phosphates of iron and aluminium is very apt to carry with it some of the calcium salt; the precipitate of the iron and aluminium obtained is not necessarily pure normal orthophosphate; and, finally, there is a great risk of intro-

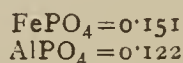
* Dissolve 100 grms. molybdic acid in 40 grms., or 417 c.c. of ammonium hydrate (sp. gr. 0.96), and pour the solution thus obtained into 1500 grms., or 1250 c.c., of nitric acid (sp. gr. 1.20). Keep in a warm place for several days, decant the solution from any sediment and preserve in glass-stoppered vessel.

ducing an error in calculating the combined phosphates of iron and aluminium over to the sesquioxides.}

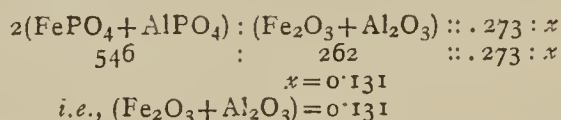
The molecular masses of the compounds concerned are:—



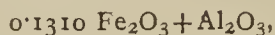
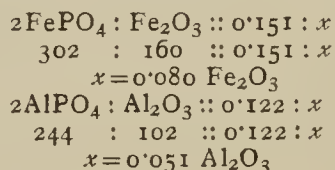
If the constituents, the iron and the aluminium phosphates, occur in the precipitate in the proportion of their respective molecular masses, *i.e.*, 151 : 122, no error will be committed in assigning to this precipitate of the mixed phosphates the formulæ $(\text{FePO}_4 + \text{AlPO}_4)$, and calculating to Fe_2O_3 , as is shown by the following example. Assume the composition of the precipitate to be—



Calculating the combined phosphates over to the combined oxides—

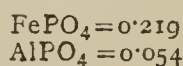


Calculating the FePO_4 and the AlPO_4 separately over to their respective oxide, and then adding them—

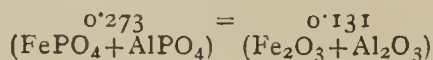


which is identical with the value previously obtained. If, however, the iron phosphate and the aluminium phosphate are present in a proportion different from the one assumed in the above example, the result obtained by calculating their combined weight to combined oxides is wrong. It will be too high or too low, accordingly as the iron or the aluminium phosphate predominates.

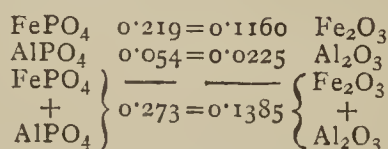
Example.—Assume that the combined phosphates weighed exactly the same as before = 0.273 grm.; but assume the composition of the precipitate to be—



Calculating the combined phosphates over to the combined oxides, of course the same result as previously found will be obtained, namely, that—

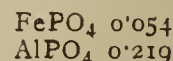


But calculating the FePO_4 and the AlPO_4 separately to their respective oxide, there is found—

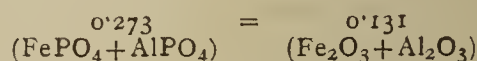


a higher result than obtained above.

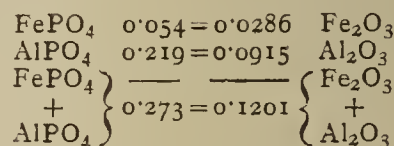
If the composition of the same weight of the combined phosphates of iron and aluminium be assumed to consist of—



there will result as before—



But,



a value considerably lower than obtained by the other method of calculation.

Method II. makes a much better showing than the preceding method. The chief objection to it is the error involved in weighing the iron and the aluminium as phosphates and calculating them to the oxides, as explained above.

This difficulty, however, could be obviated in the following manner:—

Proceed with the analysis exactly as directed, and weigh the iron and the aluminium as phosphates; then dissolve in H_2SO_4 ; reduce the iron by means of zinc and platinum in a H_2SO_4 solution; titrate with standardised $\text{K}_2\text{Mn}_2\text{O}_8$ solution, and record the iron as Fe_2O_3 ; calculate this to iron phosphate, FePO_4 ; subtract this value from the weight of the combined phosphates, and then calculate the remainder, the AlPO_4 to Al_2O_3 .

Method III. has certainly yielded the most satisfactory result, for the difference between the amount of the iron and the aluminium oxides present and determined is only 0.04 per cent, a difference corresponding to less than two-tenths of a m.grm. in the actual weight of the precipitate, $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$, in this experiment.

The feature which serves as the special endorsement of this method is the fact that the constituents sought are reported in the very form in which they are weighed, and that thus the introduction of errors by calculation is excluded.

In order to test the working of these three methods in actual practice, they were applied to the analysis of four samples of bone-black.

The results obtained follow—

Sample.	Method I.	Method II.	Method III.
1	0.65	0.47	0.47
2	0.50	0.44	0.54
3	0.58	0.41	0.46
4	0.43	0.36	0.38

—Science.

The Absorption of Hydrogen Selenide in Selenium Liquefied at a High Temperature.—H. Pélabon.—It is known that if we heat in a sealed tube a mixture of selenium and hydrogen at a temperature above 250° and for a sufficient time, these bodies combine in part, yielding hydrogen selenide. If after thus heating a tube strongly charged with selenide it is allowed to cool in motionless air, the surface of the liquid selenium becomes the seat of an escape of gas and the liquid seems to boil. As the temperature falls the escape of gas becomes less easy, and, lastly, when the selenium arrives at the state of paste some bubbles burst the surface, projecting a little selenium outwards. The gas absorbed under these conditions by liquid selenium contains large proportions of hydrogen selenide.—*Comptes Rendus*, cxvi., No. 23.

ON NICKEL-STEEL ARMOUR.

By SERGIUS KERN, M.E., St. Petersburg.

AMONGST the various types of armour-plate that are now seriously engaging the attention of artillerists is the nickel-steel plate.

The Olouchoff Steel Works, St. Petersburg, started the manufacture of such armour-plate. The first plate produced had a trial quite recently. A perfect success is reported; it behaved in the same manner as the best nickel-plate coming from the French "St. Chamond Works." All the shells rebounded after penetrating the plate to nearly the thickness of the same. The steel shells were fired from a 6-inch breech-loading gun of 35 calibres, and had an initial velocity of 2200 feet per second. The Olouchoff plate remained uninjured, and showed no cracks. It contained 3 per cent of nickel and 0.3 per cent of carbon; Siemens-Martin steel was used.

As the Olouchoff Works have no rolling-mills, the ingot cast was rolled into a plate 8 ft. \times 8 ft. \times 10 inches at the Government Kolpino Works, and sent back to the Olouchoff Works for hardening and tempering. This was successfully done by engineer Rzeshtarsky.

The first three shells fired were manufactured by the Poutiloff Works, St. Petersburg; they remained whole and showed no cracks. The last two shells fired were prepared by the Olouchoff Works; the heads remained in the plate, and the rear parts of the shells broke up into small fragments, which were scattered over the ground.

We must add that the Poutiloff shells contained chromium (about 2 per cent), and were manufactured by the Pflotzer process.

DETERMINATION OF PHOSPHORIC ACID.

By MM. A. VILLIERS and FR. BORG.

THE instructions which are found in analytical treatises and in the numerous memoirs which have been published on the determination of ammonium molybdate are very contradictory.

According to some authors the composition of the molybdic precipitate is variable, and we cannot find the weight of phosphoric acid present in the specimen from the direct weight of the precipitate. It must be dissolved in ammonia and precipitated with magnesia mixture, so as to form ammonium magnesium phosphate. According to others the composition of the precipitate is constant, and it may be weighed directly.

We have endeavoured to fix the conditions necessary for obtaining exact results.

We used the reagent of Sonnenschein and Eggertz, prepared by dissolving 150 grms. of ammonium molybdate in luke-warm water, making the solution up to 1 litre with cold water, and pouring it into 1 litre of nitric acid of sp. gr. 1.2.

We suppose, firstly, the entire absence of alumina and iron. We add an excess of the reagent—about 100 c.c. to 0.1 gm. of phosphoric acid (PO_5). The precipitation should be effected in the cold below 15° (the precipitate formed at higher temperatures is very thin, and is apt to pass through the filters). It is also well, in order that the precipitate may deposit rapidly, not to mix the reagent at once with the solution, but to let the former run carefully down the side of the beaker, and not to stir the mixture until two hours have elapsed.

In a solution of sodium phosphate the precipitation is complete in the cold after four hours. In presence of a great number of salts the precipitation is retarded, but it becomes complete after a more prolonged contact in the cold, or after four hours' digestion at about 40° . The influence of potassium salts is of the same kind, and, contrary to what has been said, it never determines an

increase of the weight of the precipitate in consequence of a partial substitution of potassium for ammonium. The retardation produced by these salts is very decided.

In all cases the precipitation may be regarded as complete by digesting a mixture prepared in the cold as above, for four hours at 40° .

A more prolonged digestion is a cause of error, in consequence of a precipitation of molybdic acid.

The precipitate is then washed by decantation and filtration with water containing one-twentieth of its volume of the molybdic reagent.

The washing must not be effected with pure water, as the precipitate then passes through the filter. It is dried with the filter for six hours in a flask with a wide mouth, which has been first weighed with the empty desiccated filter, and we ascertain that the result obtained in a second weighing is identical. The ammonium phosphomolybdate has a perfectly definite composition, 1 part containing 0.03728 phosphoric acid (PO_5).

The desiccation cannot be effected above 100° , as the paper begins to turn yellow.

Precipitation with ammonium molybdate is an excellent method for the direct determination of phosphoric acid, in the absence of iron and alumina, of silica, of organic matter such as tartaric acid, and of substances which may reduce molybdic acid, such as the iodides. The precipitation will be always complete after four hours' digestion at 40° . The precipitate will not contain an excess of molybdic acid if the digestion is not further prolonged.

In presence of aluminium and iron the phosphomolybdate may contain a notable proportion of these metals. If iron is abundant its presence is even indicated by the deeper colour.

We cannot here weigh the precipitate directly. If we re-dissolve in ammonia and precipitate with magnesia mixture (as it is recommended in most analytical manuals), we still do not get rid of iron and alumina. We obtain, on the contrary, very accurate results in the following manner:—

We effect the precipitation of the ammonium phosphomolybdate and the washing as above directed without seeking to draw the precipitate upon the filter; we then dissolve with ammonia the portion contained in the filter, causing the ammoniacal liquid to flow back upon the principal portion of the precipitate. Lastly, after complete solution, we add tartaric acid. We may thus acidify the liquid without re-precipitating the phosphomolybdate. We then render the liquid slightly alkaline with an excess of ammonia, and determine the phosphoric acid as in the ordinary manner by precipitation in the state of ammonium-magnesium phosphate. The iron and alumina remain completely in solution, thanks to the presence of tartaric acid.—*Comptes Rendus*, cxvi., p. 989.

Detection of Nitrobenzene.—J. Marpurgo (*Pharm. Post*).—The author puts in a small porcelain capsule two drops of liquefied carbolic acid, three drops of water, and a fragment of potassium hydroxide of the size of a pea. The mixture is carefully heated to boiling, and the aqueous liquid to be tested for nitrobenzene is added. After prolonged boiling there appears a crimson ring at the margin of the liquid. On adding a saturated solution of chloride of lime, this ring takes an emerald-green colour. To detect nitrobenzene in soap it is dissolved in water, mixed with an excess of milk of lime, extracted with ether, and the ethereal residue tested as above. For detecting nitrobenzene in oil of bitter almonds, the fact may be utilised that the latter, if heated with manganese peroxide and sulphuric acid, loses its specific odour and assumes transiently an unpleasant smell, which gradually disappears, whilst nitrobenzol retains its odour on similar treatment.

NOTICES OF BOOKS.

Agricultural Journal. Published by the Department of Agriculture of the Cape Colony. Vol. vi. May 18th, 1893.

THE Cape Agricultural Department is making a very vigorous effort to extend sound agricultural knowledge throughout the Colony. The Journal before us is one of the agencies employed for this purpose. We are glad to see from the "Editorial Note" that "political or personal remarks will be strictly excluded."

It is complained that in many districts crops have suffered from the drought during the earlier part of the year. Locusts have also proved very troublesome. We must therefore beg to call the attention of the Editor to the utilisation of the eggs of locusts as reported from Algeria. These eggs yield an oil valuable both for therapeutical and industrial uses.

Experiments have been made with different kinds of wheat, such as the Dakota, the Medea, and the Neapolitan. The great point in view has been resistance to rust. The results have been somewhat complicated by the circumstance that wheats which have escaped rust in one district have suffered severely in another. It is concluded that the better the soil has been cultivated, the less the crop suffers from rust.

On the important subject of manures the writers of the "Agricultural Journal" follow the example of M. G. Ville in placing lime on a level with potash, phosphoric acid, and nitrogen. It is possible that the soils of South Africa may be poorer in lime than those of Britain. Here, where lime is needed, it is added to the soil separately, and not in conjunction with other plant foods, save when it is applied in the form of superphosphate.

As regards the various guanos and other manures, we note that the analyses have been almost all executed by aliens. Our British examiners, we fear, are found unequal in practice to chemists trained on a different system.

Experiments are being made with the Australian "salt-bush," *Atriplex nummularia*, which seems to be eaten by stock in preference to the native African species, *A. halimus*, which in addition seeds less readily.

The introduction of the Australian species is chiefly due to Sir Ferdinand von Müller, the distinguished Government Botanist of Victoria, to whom South Africa is also indebted for the acclimatisation of the Eucalyptus, which is now springing up by thousands in what were formerly treeless wastes.

Vine growers will read with great interest the account of the satisfactory results obtained, both in Africa and Australia, by the use of pure ferments from the most famous French growths—Burgundies, Bordeaux, &c.

Over irrigation, according to a correspondent, has rendered some lands barren from the accumulation of saline matter. As a remedy the Editor recommends the cultivation of beet, mangolds, and asparagus, and especially of the Australian salt-bush.

Attention has been called to cool storage for fruit, in view of the successful results obtained in Australia and Tasmania. A room of 2000 cubic feet is kept cooled to an even temperature of 40° to 45° for two months, at 30s. per week, though the outside temperature was about 92°. In such a chamber oranges can be kept in excellent condition from eight to ten weeks. We feel a very warm interest in these experiments. The demand for fruit in England is almost unlimited, and we should all prefer African or Australian produce to that of America or of the European continent, especially as the former growths would come in at a time when the latter are out of season.

The Hygienic Treatment of Domestic Sewage. Peter Spence and Sons, Manchester Alum Works.

THIS pamphlet has for its subject the treatment of sewage by means of Spence's "alumino-ferric" cake. This material, a compound of aluminium and iron sulphate, has proved itself most effectual in the treatment of sewage; and on the small scale it may, as here recommended, be used without the co-operation of absorbent agents such as become necessary when certain kinds of industrial refuse are mixed with the domestic sewage.

The instructions for the size, shape, and position of the settling tanks are thoroughly sound. The importance of a free access of air and light is insisted upon on account of the demonstrated efficacy of light in destroying morbid microbia. It is sad that so simple a truth should have been neglected by the London County Council to the great loss of the metropolitan rate-payers.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvi., No. 23, June 5, 1893.

Researches on the Iron of Orisak.—Henri Moissan.—In the specimens of this iron, which M. Daubrée has placed at our disposal, we have found in one sapphire, in three amorphous carbon, in two sprouting graphite, and in one ordinary graphite, but in none of them diamonds, whether black or transparent.

Genesis of Natural Phosphates, especially those which have Derived their Phosphorus from Organised Beings.—Armand Gautier.—It is experimentally established that at least a part of the tribasic calcium phosphate and of the bibasic (brushite) results from the action upon limestone of ammonium phosphates derived in turn from the bacterian destruction of nitrogenous and phosphoric organised substances.

The Assay of Manganese Oxides by Hydrogen Peroxide.—Adolphe Carnot.—This paper will be inserted in full.

Organo-Metallic Compounds Belonging to the Aromatic Series.—G. Perrier.—In a former memoir (*Comptes Rendus*, May 15, 1893) the author has shown that anhydrous aluminium chloride combines with certain aromatic substances, acetones, aceton-phenols, ethers, and phenols. He now purposes to show that this combination is likewise effected with the chlorides of acid. To this end he has experimented with benzoyl chloride and aluminium chloride. He has studied the action of the organo-metallic compound obtained with benzoyl chloride upon the hydrocarbons and the phenols, benzoyl-diphenyl, benzoyl-retene, benzoyl-naphthol- β , and other chlorides of acids and aluminium chloride.

The Use of Vine Leaves as Cattle-Food.—A. Muntz.—The author recommends the consumption of vine leaves, after vintage, as food for cattle. In the south of France sheep are turned into the vineyard, after vintage, to consume the leaves. According to the author this practice is not injurious if the wood is thoroughly ripened. The sheep do not seem to be injured by the solutions of copper which are sprinkled over vines to destroy fungi, &c.

ERRATUM.—P. 293, col. 1, line 2 from top, for "even" read "soon."

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